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(Continued from page three of cover)

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(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 453.)

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Received Presented

TABLE OF CONTENTS

1. Introduction 327
2. Description of the Apparatus 328
(a) General 328
(b) Main Thermometer System 328
(c) Auxiliary Thermometer System 334
(d) External Pressure Control System 335
(e) Platinum Resistance Thermometers 335
(f) Thermostats 336
3. Calibrations, Tests, and Performance 336
(a) Main Thermometer System 336
(b) Auxiliary Thermometer System 340
(c) Platinum Resistance Thermometers 340
(d) Thermostats 340
4. Test of the Performance of the Auxiliary Thermometer 340
5. Filling the Gas Thermometers 341
6. Procedure for a Run 341
7. Summary 342

1. Introduction

The investigation of the properties of gases by means of gas thermometers during the first half of the nineteenth century led to the particular form of the absolute temperature scale proposed by Kelvin. At the present time the gas thermometer is recognized as the primary instrument for the determination of temperatures on the absolute scale. Two types of gas thermometer are in general use: the constant pressure instrument in which the pressure of a definite mass of gas is maintained constant and the volume of the system measured at each temperature; and the constant volume instrument in which the volume of a definite mass of gas is maintained constant and the pressure measured at each temperature. In a later paper are given the relations between the measured volumes (or pressures) and the absolute temperature for an idealized gas thermometer filled with an ideal gas; and the corrections to be applied to the observations due to the deviations of the actual from the idealized instrument and of the real thermometric fluid from an ideal gas.

The experimental difficulties encountered in gas thermometric measurements led to the adoption in 1927[1] of an International Temperature Scale which in the temperature range − 190° to + 660° C. is based on the indications of a standard platinum resistance thermometer, an instrument of high precision and reproducibility. Although the International Scale was designed to agree as closely as possible with the absolute scale, the actual deviations in the region above 0° C. are not known with any great degree of certainty.

We have constructed gas thermometers of the constant volume type for the realization of the absolute temperature scale and standard platinum resistance thermometers for reproducing the International Scale and have compared these two scales from 0° to 450° C. The apparatus, methods of calibration, and procedure used in taking the readings are described in the present paper. Our gas thermometers are the same in general design as those used by other investigators[2] with some modifications and improve-

[1] See G. K. Burgess, Bur. Standards, J. Research, **1,** 635–640 (1928).

[2] P. Chappuis, Trav. et Mém., Bureau Int., **6,** 125 + 187 pp. (1888); ibid., **13,** 66 pp. (1907); ibid., **16,** 44 pp. (1917); P. Chappuis and J. A. Harker, ibid., **12,** 90 pp. (1902); Phil. Trans. Royal Soc. London, **194A,** 37–134 (1900).

L. Holborn and A. L. Day, Am. J. Sci., (4) **8,** 165–193 (1899); ibid., (4) **10,** 171–206 (1900); Wied. Ann. der Physik, **68,** 817–852 (1899); Ann. der Physik, (4) **2,** 505–545 (1900); L. Holborn and S. Valentiner, Ann. der Physik, (4) **22,** 1–48 (1907); L. Holborn and F. Henning, ibid., (4) **35,** 761–774 (1911); F. Henning and W. Heuse, Zeit. f. Physik, **5,** 285–314 (1921); ibid., **6,**

ments which, we believe, permit the necessary corrections to be made with greater certainty than heretofore.

2. Description of the Apparatus

(*a*) *General*

A sketch of the apparatus is shown in Fig. 1. The entire system was constructed in duplicate, the individual systems being designated Red and Green for easy identification. There are three pressure systems to be considered: the main thermometer system, the auxiliary thermometer system, and the external pressure control system.

The gas thermometer bulb B of vitreous silica was connected through a graded seal to a pyrex glass capillary A'. To the top of A' was soldered a stainless steel capillary D which led to a steel T-valve F, used for evacuation of the system and introduction of pure nitrogen, and thence to the short arm G of the main mercury manometer H. The two arms G and J of the manometer, the mercury reservoir L, and the mercury injector I (used for fine adjustment of the mercury levels in the manometer) were connected with each other in a steel block, the various parts of the system being separated by steel stopcocks as shown. The manometer was enclosed in an aluminum housing which was in turn surrounded by an air thermostat K. Mercury levels were read to 0.001 mm. by means of a comparator and scale. The gas pressure in the system was adjusted to approximately 1000, 750, 600, 450, or 330 mm. of mercury when the bulb B was at 0° C.

The dead space correction for the region of large thermal gradient (the pyrex capillary A') was evaluated by use of the auxiliary gas thermometer[3] A, a pyrex glass tube placed parallel to and close beside A'. The auxiliary thermometer bulb was sealed to short lengths of glass capillary at the top and bottom. To the top was soldered the stainless steel capillary C which led to the short arm P of the auxiliary mercury manometer M. This system was evacuated, and pure nitrogen introduced through an outlet sealed to the short arm. The two arms P and Q of the manometer, the mercury reservoir T, and the mercury injector R were connected with each other in a steel block through steel stopcocks as shown. This manometer was enclosed in a steel housing but was not especially thermostated. Mercury levels were read to 0.1 mm. by means of a slider and scale S. The gas pressure in the system was adjusted to approximately 600 mm. of mercury when the bulb A was at 0° C.

The gas thermometer bulb B and capillary A', and the auxiliary thermometer bulb A were enclosed in welded steel cases connected at the top by the steel capillary E which led to the open mercury manometer N. Levels in this manometer were read to 1 mm. The external pressure control system was filled with dried commercial nitrogen and the pressure adjusted at each measurement to within 3 mm. of the pressure inside the bulb B.

(*b*) *Main Thermometer System*

Bulb, Capillaries, and T-Valve. The thermometer bulb B was made of vitreous silica by the General Electric Company and was exceptionally clear and uniform in dimensions. The bulb was a right circular cylinder 4 cm. in radius and 15 cm. long capped by two hemispheres of 4 cm. radius, the wall thickness being 2 mm. and the internal volume 1000 ml. A vitreous silica capillary 0.75 mm. bore and 4 cm. long was sealed to

215–223 (1921); W. Heuse and J. Otto, Ann. der Physik, (5) **2,** 1012–1030 (1929).

H. K. Onnes and coworkers, Physical Lab., Univ. of Leiden, Comm. Nos. **27,** 38 pp. (1896); **60,** 30 pp. (1900); **95e,** 55–67 (1906); **141a,** 1–11 (1914); **152a,** 1–17 (1917); **156a,** 1–32 (1922); **176d,** 43–52 (1925); W. H. Keesom and Miss H. van der Horst, ibid., Comm. No. **188a,** 1–15 (1927); W. H. Keesom, Miss H. van der Horst, and K. W. Taconis, Kamerlingh Onnes Lab., Univ. of Leiden, Comm. No. **230d,** 9 pp. (1933–4).

H. L. Callendar and E. H. Griffiths, Phil. Trans. Royal Soc. London, **182A,** 119–157 (1891); M. W. Travers, G. Senter, and A. Jaquerod, ibid., **200A,** 105–180 (1903); J. A. Harker, ibid, **203A,** 343–384 (1904); N. Eumorfopoulos, Proc. Royal Soc. London, **81A,** 339–362 (1908); ibid., **90A,** 189–203 (1914).

A. L. Day and J. K. Clement, Am. J. Sci., (4) **26,** 405–463 (1908); A. L. Day, R. B. Sosman, and E. T. Allen, ibid., (4) **29,** 93–161 (1910); Carnegie Institution Publication No. **157** (1911); A. L. Day and R. B. Sosman, J. de Physique (5) **2,** 727–749, 831–844, 899–911 (1912).

F. G. Keyes, B. Townshend, and L. H. Young, J. Math. Phys., Mass. Inst. Tech., **1,** 243–312 (1922).

M. Kinoshita and J. Oishi, Phil. Mag., (7) **24,** 52–62 (1937).

[3] N. Eumorfopoulos, Proc. Royal Soc. London, **81A,** 339–362 (1908) for constant pressure gas thermometer; H. K. Onnes and G. Holst, Physical Lab., Univ. of Leiden, Comm. No. **141 (a),** 1–11 (1914) auxiliary gas thermometer credited to P. Chappuis in this publication; F. Henning, *Temperaturmessung*, p. 47, F. Vieweg und Sohn, Braunschweig, 1915; P. Chappuis, Trav. et Mém., Bureau Int., **16,** 44 pp. (1917).

each end of the bulb. The graded seal was of capillary tubing 0.75 mm. bore at each end but of larger bore for a distance of about 1 cm. where the intermediate glasses were used. The pyrex capillary A' was 0.75 mm. bore and 45 cm. long, and was selected from several for uniformity of bore. The stainless steel capillaries D were 0.6 mm. bore, the shorter length (A' to F) being 30 cm. and the longer (F to G) 300 cm. in length.

of the steel capillary until it protruded into the glass tube, and solder allowed to run in at A with gentle warming until it showed at B. The steel capillary was forced against the end of the glass capillary so that contact was made. Attainment of contact was determined by measurement of the distance between index marks on the steel and glass capillaries. A study of test samples showed that solder filled all of the space between the cap

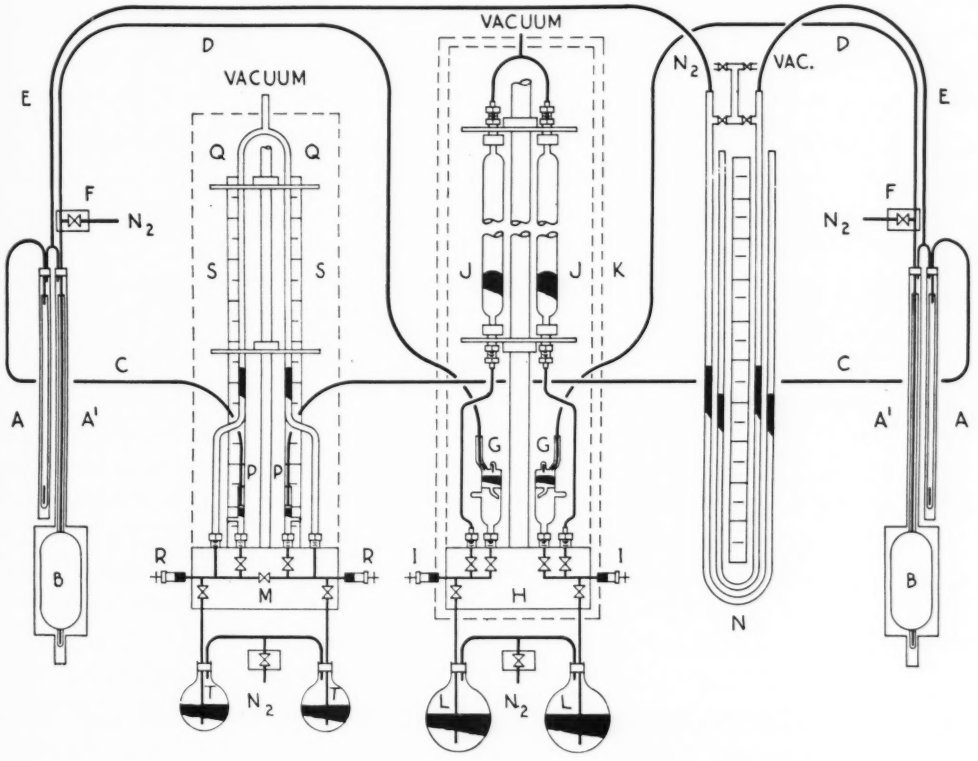
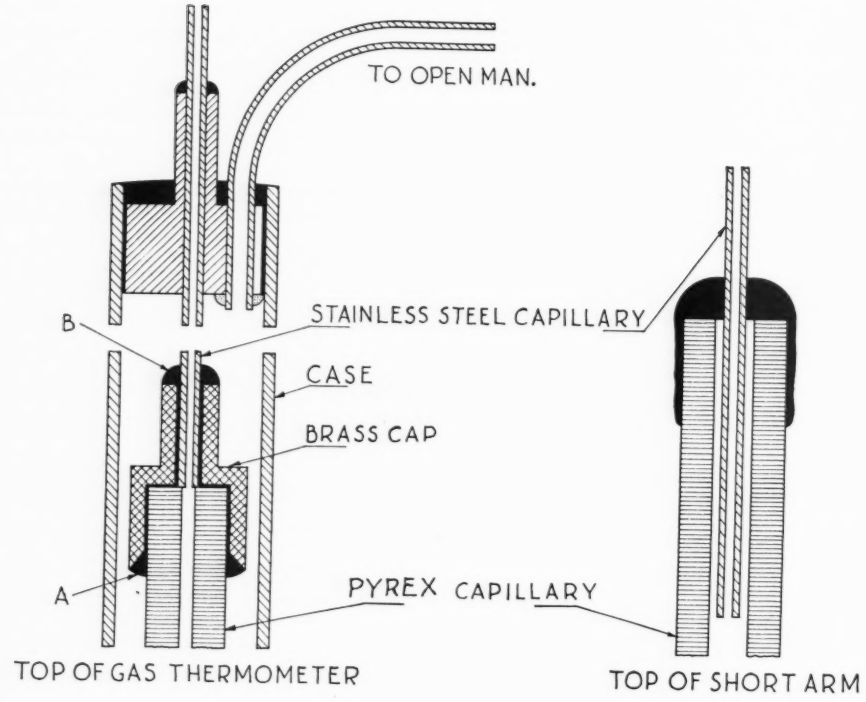


FIG. 1. Sketch of the gas thermometer system.

The glass-to-metal joint at the top of A' was made as shown in Fig. 2. The end of the glass capillary was ground perpendicular to the axis of the tube, platinized, and copper-plated. The stainless steel capillary was turned square, coated with silver solder, and tinned. A brass cap which fitted tightly on the steel capillary and was 0.1 mm. in diameter larger than the glass capillary was made. The parts were fitted together and placed with the glass tube pointing upward, a piece of piano wire was thrust through the bore and the capillaries and did not run into either tube.

The T-valve is shown in Fig. 2. The stainless steel capillaries A' and G (which led to the pyrex capillary and to the short arm of the manometer, respectively) were a tight fit in the recessed holes of the T-valve, and their ends were turned off at the same angle as that of the point of the drill used to recess the holes. The joint was soldered with silver solder. That the capillaries were seated in the holes was shown by measurement of



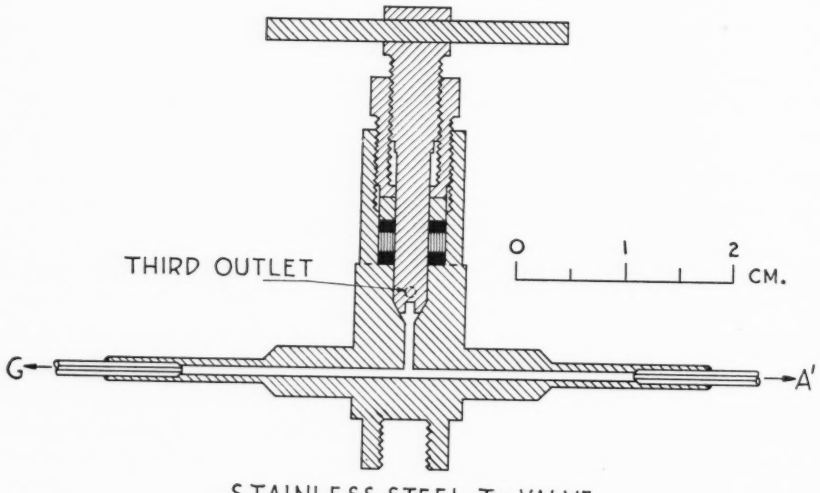


FIG. 2. Sketches of the glass-to-metal joints and the T-valve.

the distance between index marks on the capillaries and the T-valve. When the T-valve was open the gas thermometer system was in communication with the loading and evacuation system through a steel tube of 2 mm. bore soldered to the third outlet of the T-valve; when the valve was closed the gas was confined in an all steel system, no packing being exposed to the thermometric fluid.

The glass-to-metal joint at the short arm of the manometer is also shown in Fig. 2. The glass capillary was prepared as described above and the steel capillary tinned at the place where the joint was to come. The steel capillary was inserted in the glass capillary and solder flowed on with gentle warming. No solder flowed into the glass capillary.

Storage, Loading, and Evacuation System. This system, which was built in duplicate, one for each gas thermometer, is sketched in Fig. 3. The gas was stored at a pressure of one meter of mercury in the 5-liter pyrex glass bulb *A*, and was transferred to the main thermometer system by means of the mercury displacement pump *C* made of pyrex glass. Adjustment of the pressure of nitrogen in the reservoir *D* caused the mercury level in *C* to rise or fall. The storage vessel *A*, the displacement pump *C*, a mercury diffusion pump, and the steel tube from the T-valve *F* (Fig. 1) of the main thermometer system were connected with each other in the steel block *B* through steel stopcocks as shown.

Main Manometer. A sketch of the main manometer is shown in Fig. 1. The manometer arms were made of pyrex glass 21 mm. internal diameter and 1.5 mm. wall thickness.

The short arm was 10 cm. long. The closure at the top of the short arm was made by sealing off the tube and attaching without blowing two capillaries: a short capillary in the axis of the tube into which was sealed a tungsten needle 1 mm. in diameter tapered at its lower end and ground flat to a circular surface 0.5 mm. in diameter, and a larger capillary 1.8 mm. bore and 10 cm. long into which was soldered the stainless steel capillary *D* from the thermometer bulb. To the bottom of the short arm was sealed a tube 5 mm. in diameter cemented by DeKhotinsky cement into a steel nut screwed into the valve block *H*. The short arm contained a side-arm for calibration purposes and a trap constructed as shown, which was designed to prevent gas or specks of foreign material from entering the upper chamber. The axis of the short arm was made vertical to within 0.2 mm. per 10 cm. of length.

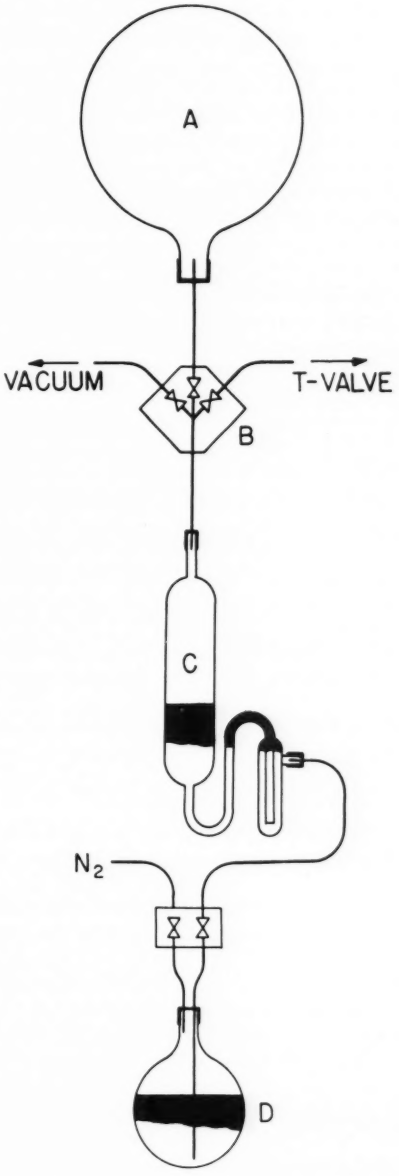


FIG. 3. Storage, loading, and evacuation system.

The long arm was 1.7 meters long and was especially selected after testing many tubes for straightness, uniformity of bore, and freedom from optical imperfections. It was sealed at the

top and bottom to tubes 5 mm. in diameter which were cemented into steel couplings, the lower being connected to the valve block by a steel capillary, and the upper to a mercury diffusion pump and McLeod gauge by copper tubes of 5 mm. bore. The axis of the long arm was made vertical to within 0.2 mm. per meter of length and in line with the axis of the short arm by adjustable clamps attached to a ground steel rod 2.5 cm. in diameter and 2.3 meters long. The bottom of the steel rod fitted into the valve block and the top was held by an adjustable pivot attached to the manometer housing. The long arms, which were slightly bowed, were placed so that the curvature was in the plane perpendicular to the line of sight of the telescopes.

The valve block *H* was of steel. The various parts of the manometer system were attached to the block by means of steel cones, connected inside the block by 0.5 mm. diameter holes, and separated by steel stopcocks similar to that in the T-valve,[4] Fig. 2. The valve block was mounted on a ball bearing turn table and base which permitted a rotation of the whole block as well as a forward and backward motion. The base was bolted to a slate block 50 by 50 by 15 cm. fitted with leveling screws; and the block rested on a steel frame work bolted to the floor. After the system had been adjusted so that all manometer tubes were the same distance from the telescopes, no further changes were made throughout the entire series of measurements.

A cast aluminum-alloy housing enclosing the manometer tubes was bolted to the valve block and held at the top by an adjustable pivot attached to a metal framework bolted to the concrete ceiling. The front and back of the housing were open. The front opening was closed by a plate glass window 1 cm. thick which was pressed gently against thin rubber gaskets glued to the machined surfaces of the housing by means of brass strips held by clamps fastened to the housing; the back was not closed. The front window was vertical to within 0.2 mm. per meter of length.

The temperatures of the mercury in the manometer and of the dead space inside the housing were determined from the readings of five short 12 ohm platinum resistance thermometers enclosed in test tubes filled with mercury and placed alternately on the right and left sides of the housing. Each thermometer was considered to read the temperature of the mercury from a point midway between it and the next lower thermometer to a point midway between it and the next higher one. The lowest thermometer was at the level of the top of the short arm and read the temperature of the short arm dead space.

The valve block and housing were enclosed in an air thermostat *K*, Fig. 1, made of 1 cm. plywood lined with 2.5 cm. of insulation. Air circulation was maintained by two fans which blew air upwards behind a false back placed 15 cm. in front of the true back and extending to within 30 cm. of the top and bottom. The fans were operated by a motor outside the thermostat and the entire unit rested on an anti-vibration mounting and did not come into contact with the air thermostat box at any place. The air passed upwards behind the false back by a cooling coil through which water from a constant feed device could be circulated, a heating coil, and a mercury-in-steel regulator containing 350 cc. of mercury; and then passed downward in front of the false back around the manometer housing. The mercury levels were viewed through movable slits 1.5 cm. high in the front of the air thermostat box. The slits were not closed by glass when the mercury levels were being measured.

The room in which the apparatus stood was thermostated, and the air stirred by a blower which drew air from the bottom of the room and delivered it to the top.

The mercury used in the manometer system was purified by electrolysis in a dilute solution of nitric acid followed by three distillations: two in a current of air and one in vacuo. It was stored in the glass flask *L*, Fig. 1, which was connected to the valve block by means of a steel capillary. The storage flask was a barometric height below the short arm of the manometer, and the mercury was forced into the manometer to the desired height by nitrogen pressure. Fine adjustments in mercury height were made by use of the steel mercury injector *I*, Fig. 1, which had a volume of 10 cc., and a piston diameter of 8 mm. The injector had an indexed head divided into 100 parts.

Illumination. For the determination of the elevation of the crown of a mercury meniscus, a beam of light[5] that behaved as parallel light with respect to vertical displacement and variation in zenith angle and as diffuse light with respect to lateral displacement and variation in azimuthal angle was directed from behind the manometer

[4] For details of the cone joints and stopcocks, see F. G. Keyes, Proc. Am. Acad. Arts Sci., **68**, 505–564 (1933).

[5] S. C. Collins and B. E. Blaisdell, Rev. Sci. Instr., **7**, 213–214, 359 (1936).

tube into the telescope of the comparator. The optical system, Fig. 4, consisted of a 6-volt flashlight bulb, a rectangular slit 0.75 mm. high by 2.5 cm. wide covered with a sheet of thin paper and at the principal focus of a cylindrical lens of 5 cm. focal length placed with the elements of the cylinder horizontal, and two rectangular apertures: one 6 mm. high by 2.5 cm. wide between the slit and the lens, and one (the exit pupil) 3 mm. high by 2.5 cm. wide in front of the lens. The system was enclosed in a brass box painted flat black on the inside. The mount carrying the lens could be moved along the long axis of the box and the distance from the lens to the slit was adjusted so that the beam of light was 3 mm. high at 1 meter distance from the front of the box. The box was fastened to a carriage mentioned below and so tilted that the beam sloped upwards toward the telescope at an angle of about 10 minutes to the horizontal. This was accomplished as follows: the telescope was leveled, the horizontal hair-line set on the axis of the telescope, the telescope itself moved so that intersection of the horizontal and vertical hair-lines rested on the crown of the meniscus, and the zenith angle of the beam varied until the shadow of the crown on a white card placed immediately in front of the objective fell about 2 mm. above the axis of the telescope.

The two optical systems, one for each manometer, were rigidly attached to a carriage moving on two vertical drill rods 2 cm. in diameter placed 7.5 cm. behind the back of the aluminum housing but inside the air thermostat. A counterweight attached to the carriage by a cord passing over pulleys fastened to the ceiling of the room permitted the observer to move the optical system so as to illuminate the meniscus in either the long or the short arm of a manometer. In Fig. 4 the carriage and one optical system is shown.

The vertical height of the beam of light could be decreased farther by brass shields painted flat black and shaped to fit the back half of the manometer tubes. Each shield was 7.5 cm. long. It had an apron 0.5 cm. wide along each vertical edge and a slot 1 cm. square in the bottom which permitted light to pass through the central portion of the manometer tube only (see Fig. 4). The shields were connected to counterweights similar to those for the optical systems except that each shield had a separate counterweight.

For the determination of the elevation of the bottom of the meniscus, diffuse light coming from in front of the manometer tubes was used. The optical system consisted of a 6-volt flashlight bulb enclosed in a small metal box with the side facing the manometer tubes consisting of a frosted glass window 2 cm. high by 1 cm. wide. The window was placed with its vertical centerline symmetrical with respect to the axes of the two manometers and at a distance of 16 cm. in

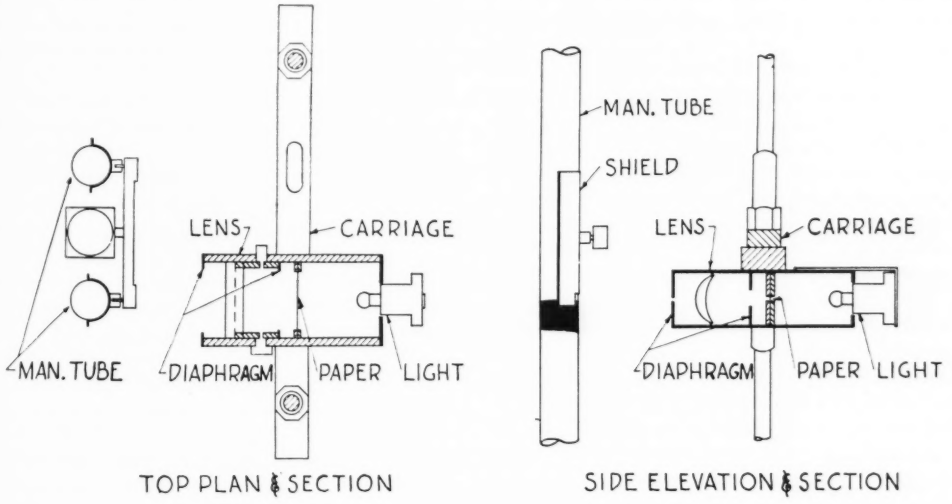


FIG. 4. Optical train for illumination of the mercury meniscus.

front of each axis. The box was rigidly attached to the mechanism that operated the movable slit (in the front of the air thermostat) and the horizontal centerlines of the window and slit were at the same elevations, the optical system and slit moving up and down together. There were two such lighting systems: one for the two long arms and one for the two short arms of the manometers. At each measurement the horizontal centerline of the window and the axis of the telescope were approximately in the same horizontal plane as the crown of the mercury meniscus.

The room was darkened for all measurements. All lamps for illumination of the menisci were turned off except when necessary for an observation.

Comparator and Scale. The two-meter Société Genevoise comparator had an invar bar to which the two telescope carriages could be rigidly clamped by means of split collars and tightening screws. One turn of the micrometer drum of the filar eye-piece of the telescope corresponded to 1 ± 0.001 mm. on the scale. The drum was divided into 100 parts. The two-meter scale was graduated into fifths of millimeters.

The comparator and scale hung from universal joints and were held at the bottom in adjustable bearings, the suspensions being attached to heavy H-beams. The bottoms of the H-beams were bolted to slate blocks fitted with leveling screws and the tops connected to the steel framework, mentioned earlier, by an adjustable pivot. The bar of the comparator and the scale were not out of the vertical by as much as 0.2 mm. per meter of length. The scale was the same optical distance from the telescopes as the axes of the manometer tubes, about 62 cm.

The scale was illuminated by spotlights, attached one to each telescope carriage. The temperature of the scale was measured by a mercury thermometer suspended at the midpoint.

Measurement of Dead Space Temperatures. The temperatures of the stainless steel capillary D and the T-valve were measured by means of four mercury thermometers.

(c) *Auxiliary Thermometer System*

Bulb and Capillary. The auxiliary thermometer bulb A, Fig. 1, was a pyrex glass tube 5 mm. bore by 45 cm. long with a short length of capillary tubing 0.5 mm. bore sealed to each end. The lower capillary was sealed off and the upper one soldered by the same method used for the main thermometer to a stainless steel capillary C, 0.6 mm. bore and 2 meters long, which led to the short arm P of the auxiliary manometer M. The bulb A was selected from several five foot lengths of glass tubes after calibration, and fulfilled the condition that the ratio of the area of the pyrex capillary A' to that of the bulb A in each horizontal plane was constant to within $\pm 0.5\%$. The elimination of the error introduced by this variation is taken up in a later paper.

The glass-to-metal joint at the short arm of the manometer was similar to that in the main manometer system.

Loading and Evacuation System. The system was evacuated through a glass tube sealed to the short arm of the manometer. This tube could be brought into communication with the auxiliary thermometer system by lowering the mercury level in the short arm. A two-way glass stopcock connected the system to a mercury diffusion pump or to a supply of commercial nitrogen which had been passed through a liquid air trap.

Auxiliary Manometer. A sketch of the auxiliary manometer is shown in Fig. 1. The manometer arms were of pyrex tubing 5 mm. bore. To the top of the short arm P was sealed a 10 cm. length of capillary 0.3 mm. bore which was sealed at its top to a 1 cm. length of capillary 1.8 mm. bore to receive the end of the stainless steel capillary C. The bottom of the short arm was cemented into a nut screwed into the valve block. Near the top of the short arm was an index mark completely encircling the tube to which the crown of the meniscus was brought in all measurements.

The long arm Q was selected for straightness, uniformity of bore and freedom from optical defects. Its axis was made vertical over the working range and in line with the axis of the short arm by adjustable clamps attached to a central steel rod.

The valve block and manometer housing were similar in construction to those of the main manometer. Since mercury heights were to be read to only 0.1 mm. the front was not closed by a glass plate and the temperature of the mercury was determined by a mercury thermometer placed inside the housing.

Mercury heights were read on a meter stick attached to the central steel rod. A slider having a fine hair-line and a device for eliminating parallax moved on the meter stick and permitted reproducible reading of the crown of the meniscus

to 0.1 mm. Diffuse light was used for illluminating the mercury meniscus. The determination of the capillary depression correction is described in a later section.

The mercury storage vessel T and the mercury injector R were similar to those for the main manometer.

Measurement of Dead Space Temperatures. The temperature of the capillary C was measured by means of a mercury thermometer.

(*d*) *External Pressure Control System*

This system eliminates the strain of the thermometer bulbs caused by large differences between the internal and external pressure and also prevents possible diffusion of gas through the bulbs. The main thermometer bulb, pyrex capillary and short length of stainless steel capillary as well as the auxiliary thermometer bulb and a short length of its capillary were enclosed in welded steel cases shown in Fig. 1. Each case was closed at the top, where the steel capillary passed through, by a brass plug and soft solder as indicated in Fig. 2. The auxiliary thermometer case was placed parallel and close to the stem of the main thermometer case. The two cases of one thermometer system were connected at the top by a steel capillary E which led to an open manometer N shown in Fig. 1. This system was filled with dried commercial nitrogen and the pressure adjusted at each measurement to within 3 mm. of the pressure in the main thermometer system. The pressure in the external system was read to 1 mm. of mercury.

The pyrex capillary A', Fig. 1, and the auxiliary thermometer bulb A were wrapped at two places with sufficient asbestos cord to make a tight fit in the steel tubes of the cases.

The gas thermometer bulb B was supported by two large soft springs, one resting on the bottom of the metal case and one on the top. These kept the bulb centered in the case and allowed for differences in thermal expansion between the pyrex capillary A' and the metal tube surrounding it.

(*e*) *Platinum Resistance Thermometers*

Construction. Three types of standard platinum resistance thermometers were made: the Callender mica-cross type and the Bureau of Standards strain-free type were used to realize the International Temperature Scale; the calorimetric or flat type was used for regulation of the thermostat temperature. The methods of construction have been described.[6] All thermometers were of the four-lead potential type and had ice-point resistances of about 25 ohms.

Annealing. Before the platinum wires were wound on the mica frames they were raised to a dull red temperature for 30 seconds by the passage of an electrical current (200 cm. of 0.1 mm. diameter wire can be connected directly across the 110-volt terminals). For some of the thermometers the heating was carried out in air; for others, in an atmosphere of nitrogen. The exclusion of oxygen seemed to have no effect on the subsequent behavior of the thermometer.

The mica-cross and strain-free windings were enclosed in pyrex glass cases protected by metal tubes and the flat type enclosed in metal cases; and the cases evacuated and filled with nitrogen to two-thirds of an atmosphere. The thermometers were annealed by being immersed in a nitrate bath (as used in the high temperature thermostat) at a temperature of 470° (or 480° C.) for two days, then at 500° C. for one day, and then at 470° (or 480° C.) until annealed. Each day the thermometer was removed from the nitrate bath, immersed in liquid air for 15 minutes, and the ice-point resistance measured. A thermometer was considered satisfactorily annealed when a 22-hour period at 470° C. and 15 minutes in liquid air caused a change in ice-point resistance less than 5×10^{-5} ohms (5×10^{-4}° C.). The mica-cross and strain-free thermometers annealed in about 6 days; the flat type did not anneal satisfactorily and was used only as a temperature regulating thermometer.

Bridge, Commutator, and Selector. The Mueller thermometer bridge[7] was made by The Eppley Laboratories, Inc.[8] It was of the oil immersion type and was thermostated at 28 ± 0.005° C. The bridge read directly to 10^{-5} ohms (approximately 10^{-4}° C. on a 25 ohm thermometer) and a variation of 10^{-5} ohms in the bridge setting caused a deflection of 0.2 to 0.5 mm. of the image of the hair-line on the scale. The ratio arms could be balanced against two built-in 25 ohm coils which could themselves be adjusted to equality. The commutator was built into the bridge and the selector was similar to that described before[6] except that mercury cups were used instead of binding-posts.

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[6] J. A. Beattie, D. D. Jacobus, and J. M. Gaines, Jr., Proc. Am. Acad. Arts Sci., **66,** 167–184 (1930).

[7] E. F. Mueller, Bull. Bur. Standards, **13,** 547–561 (1916–17).

[8] M. Eppley, Rev. Sci. Instr., **3,** 687–711 (1932).

All measurements were made with a battery current of 0.002 ampere through the thermometer coil and 30 seconds after depression of the battery key. The heating effect was measured at each temperature at which the thermometer was used and found to be 0.001° C. at 0° C., 0.0008 at 150°, and 0.0004 at 444.6°.

(*f*) *Thermostats*

Two thermostats were used: one for the range 0° to 150° C. was filled with oil, and the other for 150° to 450° was filled with the eutectic mixture of lithium, sodium, and potassium nitrates. The thermostat vessels[9] and stirring mechanism[10] have been described before. When the oil thermostat was used at 0° C., kerosene was circulated by a pump through copper coils immersed in a salt-ice mixture and then through the large steel coil[9] in the thermostat vessel.

A fan blew air across the top of the thermostat in the direction away from the main manometer.

The method of regulation of the temperature of the thermostats has been previously described.[11]

3. Calibrations, Tests, and Performance

(*a*) *Main Thermometer System*

Volumes. The volume of the main thermometer bulb was determined from the mass and density of air-free conductivity water contained at 0° C. and one atmosphere pressure inside and outside. The average deviation of three determinations of the volume of a bulb from the mean was less than 0.3×10^{-6} liter.

The coefficient of linear thermal expansion of the material of the bulb from − 190° to + 450° C. was determined from a ring prepared from one of the bulbs after the completion of all gas thermometer measurements. The ring was given the same heat treatment as that given the bulb.

The stretch of the bulb caused by a difference between inside and outside pressure and the coefficient of cubical compressibility of vitreous silica were determined at 25°, 100°, 200°, and 300° C. by a method described in a later paper.

The bulbs were tested for temperature hysteresis: (1) by determination of the volume at 0° C. before and immediately after heating to 450° C. for one day; (2) by measurement of the thermal dilation of mercury in the bulb as described in a forthcoming paper; (3) by measurement by an interference method of the thermal linear expansion of a ring made from one of the bulbs. All three methods indicate that the bulbs did not assume their equilibrium volume at any temperature within 2 hours after being at a quite different temperature but that after being thermostated 6 hours at any temperature the equilibrium volume had be enreached to within 0.3×10^{-6} liter.

The bulbs were tested for pressure hysteresis at 0° and 444.6° C. by the determination of the corrected gas pressure in the bulb (the pressure in the steel case being the same as that in the bulb), evacuation of the case, refilling the case after six hours with nitrogen to the original pressure, and then redetermining the corrected pressure in the bulb. No pressure hysteresis in the range 0 to 2 atm. was found.

This test also proved that the assembly enclosed in the case was free from leak. In the preliminary evacuation of the main gas thermometer system the pressure was followed for a period of a month for a part of which time the bulbs were at 500° C.

The volume of all vitreous and steel capillaries were originally determined from the mass and density of mercury contained. The area of the pyrex capillary *A′*, Fig. 1, was determined at each centimeter from the length (corrected for the volumes of the menisci at each end), mass, and density of a thread of mercury 2 cm. long, the thread being moved along 1 cm. at a time. The volume of the T-valve was originally computed from the known dimensions.

When the main manometer had been set up, the area of the short arm just below the tip of the tungsten needle and the volume from a plane through the tip of the needle to the top of the glass capillary (at *G*, Fig. 1) were determined by the withdrawal of mercury through a side arm, and also by forcing mercury into the evacuated short arm from the calibrated injector *I*. In these measurements the same method of illumination and reading of the height of the meniscus was employed and the same table of meniscus volumes used as in the gas thermometric runs. The diameter of the long arm of the manometer at various heights was determined by similar methods.

The volumes resulting from the above methods were used in the preliminary reduction of the measurements. For the final computations volumes determined in the following manner were used.

[9] J. A. Beattie, Rev. Sci. Instr., **2,** 458–465 (1931).

[10] S. C. Collins, Rev. Sci. Instr., **7,** 502 (1936).

[11] J. A. Beattie, Proc. Am. Acad. Arts Sci., **69,** 389–405 (1934).

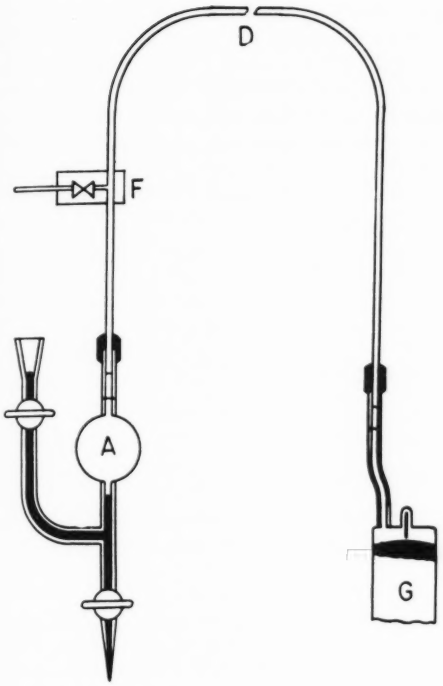

FIG. 5. Gas expansion apparatus for determination of dead space volumes.

After the completion of all of the gas thermometric runs the steel capillary D, Fig. 1, was cut just above the soldered joint at the top of A' and the volume of the part of the dead space in the steel capillaries, the T-valve, and the short arm of the manometer (that part of the main thermometer system at room temperature) determined in one portion by a gas expansion method.[12] The apparatus is sketched in Fig. 5. A pyrex glass bulb A, having a volume about $\sqrt{2}$ times that of the system to be determined, was cemented to the end of the steel capillary. The system was evacuated through the T-valve, the bulb A filled with mercury, and nitrogen introduced through the T-valve until the pressure was approximately 1200 mm. The pressure was then read on the main manometer; the mercury was run out of the bulb A into a weighing bottle; and the pressure read again. Since the number of moles N of nitrogen was the same at both measurements and the temperature was constant to 0.01° C. during a measurement:

$$N = \frac{p_1 V_1}{RT + Bp_1} = \frac{p_2 (V_1 + \Delta V)}{RT + Bp_2}, \qquad (1)$$

or, if T may be considered constant:

$$p_1 V_1 = p_2(V_1 + \Delta V) + \frac{Bp_1 p_2}{RT} \Delta V, \qquad (2)$$

where

$$V_1 = V_d + V_{s_1} + V_A, \qquad (3)$$

$$\Delta V = (V_{s_2} - V_{s_1}) + V_{Hg}. \qquad (4)$$

Thus

$$V_d = \frac{p_2}{p_1 - p_2} V_{Hg} - V_A + \frac{1}{p_1 - p_2}(V_{s_2} p_2 - V_{s_1} p_1) + \frac{p_1 p_2}{p_1 - p_2} \frac{B}{RT}(V_{s_2} - V_{s_1} + V_{Hg}). \qquad (5)$$

In the above relations:

p_1 = initial pressure
p_2 = final pressure
T = Kelvin temperature
B = second virial coefficient for nitrogen at T.
V_d = volume of dead space from end of the steel capillary D to a horizontal plane through the tungsten tip in the short arm.
V_s = volume in short arm from a horizontal plane through the tungsten tip to the mercury surface (the volume of a cylinder of height equal to the distance from the tungsten tip to the crown of the meniscus plus the covolume of the meniscus). Subscripts 1 and 2 denote this volume in the initial and final measurement, respectively.
V_A = volume in A during the initial pressure measurement (the volume of the annular space around the steel capillary plus the volume of a cylinder of height equal to the distance from the end of the steel capillary to the crown of the mercury meniscus plus the covolume of the meniscus).
V_{Hg} = volume of mercury run out of A.

[12] A somewhat similar method was used by L. Holborn and S. Valentiner, Zeit. f. Instr., **28,** 105 (1908); L. Holborn and F. Henning, Ann. der Physik, (4) **35,** 761–774 (1911); A. L. Day and R. B. Sosman, Am. J. Sci., (4) **33,** 517–533 (1912); P. Chappuis, Trav. et Mém., Bureau Int., **16,** 44 pp. (1917); P. G. Cath and H. K. Onnes, Physical Lab., Univ. of Leiden, Comm. No. **152a,** 1–17 (1917).

The steel capillary D was then unsoldered from the short arm of the main manometer, and the volume in the short arm itself determined by the gas expansion method outlined above, a short length of calibrated steel capillary being used to connect A and the short arm.

The capillary D was cut on each side of the T-valve and the volumes of the three parts of the dead space so produced determined in a separate apparatus by a gas expansion method.[13]

Thus the volume of the portion of the dead space at room temperature was determined in three separate experiments: (1) before the gas thermometric runs by the mass and density of mercury contained in the separate parts; (2) after the gas thermometric runs in a single portion by a gas expansion method, and (3) in four portions by a gas expansion method. Method (1) gave too small values of the volumes for all steel parts and correct volumes for glass parts of the apparatus. This effect has been discussed in another publication.[13] For both gas thermometric systems methods (2) and (3) agreed to 5×10^{-6} liter or better. Method (2) was taken to give the correct dead space volume.

The capillary A', Fig. 1, was cut between the bulb B and the graded seal and its volume (which included a portion of vitreous silica capillary, the graded seal, the pyrex capillary, the metal to glass joint, and a short portion of steel capillary) determined by a gas expansion method.[13] Since most of this system was of vitreous material, the volume so determined agreed well with that measured before the gas thermometric runs from the mass and density of mercury contained.

Elevations. The methods used for determining the elevations of the crown and bottom of a mercury meniscus were tested for error before and after the gas thermometer measurements. Sources of error investigated were: (1) the scale, (2) the comparator, (3) the plate glass, (4) the manometer tubes, and (5) the lighting system.

The scale was calibrated at the U. S. National Bureau of Standards. Frequently during the measurements the filar micrometers of the comparator were run over all divisions within 2 mm. of those used. This served to check the calibration of the scale and also the thread of the micrometer. Apparent errors greater than 0.002 mm. were never found.

The bar of the comparator was made vertical by sighting with the telescopes on three plumb lines arranged 120° apart. The optical axis of the objective of the telescopes did not coincide exactly with the mechanical axis. Both objectives were turned so that the displacement of the image was in the horizontal plane. The positions of the scale and manometer tubes were carefully adjusted and the objectives of the telescopes focused so that the images of the rulings and crowns of the menisci were in the vertical planes of the hair-lines, and thereafter no changes were made during all runs and calibrations. The eyepieces were refocused on the hair-lines and the telescopes leveled when necessary. The vertical cross-hairs of the telescopes were made parallel with the vertical line on the scale. At various times the elevation of the same mercury surface was read by each of the two telescopes. No systematic difference was found.

The errors due to optical defects in the plate glass front and in the manometer tubes were investigated throughout the runs. Such errors may arise because: (1) the inner and outer walls are parallel but not vertical; and (2) the two walls are not parallel. The error due to the first effect is small and easily calculated: each part of the system was set up so that the error was less than 0.001 mm. The error caused by a wedge in the glass could not be evaluated directly. The effect in the plate glass was proved negligible by measuring the thickness of the glass at various points and by viewing the scale through the plate glass. The effect in the manometer arm both long and short were studied: (1) by measurement of the distance between lines on a scale hung inside the glass tube so as to coincide with the axis of the tube; (2) by measurement of the apparent displacement of the center of a fine wire stretched behind the manometer tube with respect to the ends of the wire, and (3) by measurement of the same pressure (produced in the manostat[14]) with the two manometers. After the gas thermometric runs the tops of the short arms were cut off and a scale inserted with one graduation outside and the other inside the tube at the height of the position of the tungsten tip. The distance between marks (about 1 mm.) was read on the telescope when the scale was directly behind the front wall of the tube and then when the scale was in the axis of the tube. In all of these tests errors as large as 0.005 mm. were seldom found and in general the errors were of the order

[13] J. Kaminsky and B. E. Blaisdell, Rev. Sci. Instr., **10**, 57–58 (1939).

[14] J. A. Beattie, M. Benedict, and B. E. Blaisdell, Proc. Am. Acad. Arts Sci., **71**, 327–360 (1937).

of 0.003 mm. which was well within the precision of the methods used.

A study of the effect of various methods of illumination of the crown and bottom of a meniscus on the apparent elevations will be presented in a forthcoming paper. The method of illumination of the crown described in a previous section of the present paper is the most satisfactory investigated. An experienced observer could read the elevation of the crown with this method of lighting with a probable error of a single observation of 0.001 mm. (5 readings). The apparent elevation was independent of: (1) the relative elevation of the axis of the telescope and the crown provided the image of the crown could be seen, (2) vertical displacement and variation in zenith angle of the optical system provided the beam of light did not slope downward to the telescope, (3) lateral displacement and variation in azimuthal angle of the optical system, (4) height of the bottom of the shield above the crown or indeed whether or not a shield was used, and (5) interchange of the two optical systems.

With the method of illumination of the bottom of the meniscus used, the height of the meniscus could be read with a probable error of 0.005 mm. (5 observations) provided the elevation of the telescope was not changed. However, as will be discussed in a later paper, the apparent elevation of the bottom (and hence height of the meniscus) determined by this method of reading is a linear function of the vertical distance from the axis of the telescope to the horizontal plane determined by the bottom of the meniscus. In our measurements this distance was 1.8 ± 0.1 mm. for the short arms of the manometers and 1.2 ± 0.5 mm. for the long arms. The measured heights of menisci in the short arm were about 1.8 mm. and were too large by 0.033 ± 0.002 mm.; those in the long arm were about 1.2 mm. and were too large by 0.024 ± 0.008 mm. The corresponding correction to the capillary depression correction in the short arm is -0.0005 ± 0.0000 mm. and that in the long arm -0.0005 ± 0.0002 mm. so that the net systematic error in capillary depression correction caused by the method of reading menisci heights is 0.0000 ± 0.0002 mm. The correction to the meniscus covolume in the short arm is $-(2.3 \pm 0.1) \times 10^{-3}$ ml. Since the same method of illumination was used for the calibration of dead space volumes as for the gas thermometric measurements the systematic error 2.3×10^{-3} ml. cancels leaving as a random error 0.1×10^{-3} ml.

Temperatures. All mercury thermometers were calibrated in the range used against platinum resistance thermometers.

The temperature of the room varied about 0.2° C. from floor to ceiling and remained constant to about 0.1° C. during a run. The short length of steel capillary and T-valve were directly over the top of the thermostat and the temperature of these parts of the dead space was about 2° C. higher than those further removed from the bath for the high temperature runs.

The air thermostat surrounding the mercury column was maintained at a temperature 1° to 2° C. higher than that of the room. Inside the aluminum housing the temperature from top to bottom varied about 0.02° C. and remained constant to 0.01° C. during a run. In most of the runs temperature conditions were better than those described above; in a few they were worse.

Surface Tension of Mercury. Keesom, van der Horst, and Taconis[15] determined the volumes of mercury menisci from X-ray shadowgraphs of the menisci taken at each measurement. We computed the capillary depression and volumes of menisci from the diameter of the tube, height of the meniscus, and the capillary constant of mercury. The latter was determined from X-ray shadowgraphs of the menisci in both short arms and both long arms of the manometer after the completion of the gas thermometer runs. Photographs were taken for several positions of the menisci and for several meniscus heights in all tubes. The x and y coordinates were measured on an astronomical plate-measuring machine at the Harvard Observatory. Blaisdell[16] has integrated by numerical methods Laplace's equation for the surface of equilibrium of a fluid in a gravitational field for 40 values of the parameter and has prepared tables of the coordinates, capillary depressions, and meniscus volumes. From these tables and the measurements of the shadowgraphs it was possible[17] to determine the capillary constant and hence the surface tension of the mercury in our manometers. The values of the capillary constant a for mercury were 0.268 ± 0.001 cm. and 0.264 ± 0.001 cm. for the two short arms of the manometer at 27° C. The

[15] W. H. Keesom, Miss H. van der Horst, and K. W. Taconis, Kamerlingh Onnes Lab., Univ. of Leiden, Comm. No. **248a,** 1–5 (1937).

[16] B. E. Blaisdell, J. Math. Phys., M. I. T., **19,** 186–245 (1940).

[17] J. A. Beattie, B. E. Blaisdell, and J. Kaye, Proc. Am. Acad. Arts and Sci., **74,** 389–397 (1941).

average, 0.266 cm., corresponds to a surface tension of 469 dynes per cm. at 27° C. The capillary constants of the mercury in the long arms were 0.248 ± 0.001 cm. and 0.249 ± 0.001 cm. The lower value was accounted for by the fact that after run No. 379 the mercury in the long arms was fouled because of a leak in the system for evacuation of the long arms.

(*b*) *Auxiliary Thermometer System*

The dead space volumes of the auxiliary gas thermometer used in the final computations were determined by the gas expansion method. The mean difference between the capillary depression of the mercury in the long and short arm of the manometer was determined in a series of experiments and this correction applied to all readings. No attempt was made to compute the capillary depression, or determine the capillary constant of mercury as was done for the main manometer.

(*c*) *Platinum Resistance Thermometers*

The platinum resistance thermometers were calibrated at the ice, steam, mercury boiling, and sulphur boiling points. The methods of realization of these points and the relations for the effect of pressure on the equilibrium temperature have been published.[18]

The ice point resistance of each thermometer was determined each day. The thermometers were calibrated at the other three fixed points every three months or so. Immediately after calibration the maximum difference from the lowest to the highest reading of the four thermometers was 0.001° C. or less when immersed in the same thermostat. As time went on the readings began to diverge and when the maximum difference became 0.003° C. the thermometers were recalibrated. In general the use of the new α and δ obtained in a calibration did not cause a difference of more than 0.001° C. in the indication of a thermometer from that computed by the α and δ of the preceding calibration.

The agreement of the four thermometers on the value of a given temperature is indicated by the following: in the runs from 0° to 150° C. the mean for all runs (Nos. 111 to 251) of the average deviation of the four thermometers from the mean value in the oil bath was 0.0007° C.; in the runs from 150° to 444.6° C. in the nitrate bath this mean for all runs (Nos. 252–394) was 0.0019° C.

Each morning the balance of the ratio coils of the bridge was tested, adjustment being made if necessary and the "zero balance"[7] of the bridge determined and subtracted from all readings made that day. The N and R readings were each taken with the battery current in the direct and reverse direction.

The short platinum resistance thermometers inside the aluminum housing were calibrated before and after the gas thermometer runs. The constants of the thermometers did not change by amounts great enough to affect their indications by 0.001° C.

The thermometer bridge was calibrated every two years in terms of one of the 100 ohm coils. The corrections changed very little with time and were determined for any month by linear interpolation between calibrations.

(*d*) *Thermostats*

The performance of the thermostats is indicated by the figures given in the preceding section. In general four thermometers after calibration agreed on the temperature of the bath to within ± 0.001° C. and this was checked by placing one thermometer in the four positions occupied by the four thermometers during a run. In the oil bath at 150° C. the agreement was not so good, being ± 0.002° C. This was due to insufficient insulation of the top of the bath; an effect which was eliminated in the nitrate bath.

The temperature of the thermostat did not vary more than 0.002° C. (usually not more than 0.001° C.) during the one hour required for a run.

4. Test of the Performance of the Auxiliary Thermometer

The theory of the use of the auxiliary thermometer as a means of determining the mean reciprocal temperature of that portion of the dead space in the region of large thermal gradient will be given in a later paper. The requirements to be fulfilled are: (1) the ratio of the area of the capillary A' of the main thermometer system to that of the bulb A of the auxiliary thermometer should be independent of height and of temperature (each tube being at the same temperature); and (2) the temperature of A' should be the same as that of A at each horizontal plane.

The failure of the apparatus to satisfy the first condition exactly can be eliminated when the temperature distribution along A' and A are

[18] J. A. Beattie, T.-C. Huang, and M. Benedict, Proc. Am. Acad. Arts Sci., **72,** 137–155 (1938); J. A. Beattie, M. Benedict, B. E. Blaisdell, and J. Kaminsky, ibid., **71,** 327–385 (1937).

known. In order to determine this distribution and to determine the errors of all simplifications made in the formulae, the temperature along A' was measured by use of seven thermocouples and the mean reciprocal temperature measured by means of the auxiliary thermometer for thermostat temperatures of 444.6° and 180° C. From a plot of temperature against distance the temperature of A' at the middle of each one-centimeter interval was read off and the dead space correction evaluated as a sum of 45 terms. The corrections were also evaluated from the indications of the auxiliary thermometer. For a thermostat temperature of 444.6° C. and a pressure of 1600 mm. in the bulb of the main thermometer, the error in the dead space correction for the gas in A' obtained by the use of the mean reciprocal temperature indicated by the auxiliary thermometer was 0.003 mm. of mercury; for a bath temperature of 180° C. and a pressure of 1000 mm., the error was 0.0005 mm.

5. Filling the Gas Thermometers

Preparation of the Nitrogen. Pure synthetic ammonia was distilled back and forth between two bulbs, the head and tail portions being discarded. After each distillation the ammonia was frozen with liquid air and pumped to a flat gauge. The ammonia vapor was then passed over a catalyst at 500° C. to decompose it into its elements, then over copper oxide at 550° C., traps for removal of water, finely divided nickel at 700° C., and finally through a tube filled with chabazite at − 78° C. The purified nitrogen was finally drawn through a liquid air trap and pumped into the bulb A of the storage system, Fig. 3.

Spectrograms of the nitrogen and of the same gas to which various known amounts of oxygen and hydrogen were added showed that the nitrogen prepared by this method contained less than 0.05 mol percent oxygen and less than 0.05 mol percent hydrogen. Analysis of the gas after the completion of the thermometric measurements gave the same results.

Preparation of the Bulbs. After the thermometric system had been completely assembled, the bulbs were heated to 500° C. and evacuated for two days through the T-valve. The pressure was then 0.009 mm. of mercury 12 hours after pumping was stopped and was increasing at the rate of 0.0002 mm. per hour, the bulbs being at 500° C. The bulbs were then filled with pure nitrogen to a pressure of 1 mm. and the system again evacuated for one week with the bulb at 500° C. This process was repeated two times, so that the bulbs were evacuated for over three weeks while at 500° C.

Loading the Bulbs. In order to adjust the ice point pressure of the thermometer, the bulb was cooled to 0° C., the gas pumped into the system by use of the mercury displacement pump, Fig. 3, until the corrected pressure was within 1 mm. of the desired value and the T-valve closed.

6. Procedure for a Run

General. The two gas thermometers filled with nitrogen to the same ice point pressure and four platinum resistance thermometers were placed in the thermostat, regulated to within a few thousandths of a degree of some even International temperature, and the indications of each instrument measured.

The range from 0° to 150° C. was first investigated, the oil thermostat being used. Readings at 0°, 25°, 50°, 75°, 100°, and 150° C. were taken for most of the ice point pressures of 1000, 750, 600, 450, and 333 mm. of mercury. Many more readings were taken at 0° and 100° C. than at other temperatures. The intermediate temperatures were approached from above and from below. The 150° C. readings were not taken at the 1000 mm. loading.

All the thermometers were then transferred to the nitrate bath. Readings were made at 150°, 200°, 250°, 300°, mercury boiling point, 400°, sulphur boiling point for each of the ice point pressures 600, 450, and 333 mm. of mercury. Most attention was given to the 150° and the sulphur boiling point; the other temperatures were approached from above and below. The corrected pressures in the gas thermometers at 150° C. were adjusted to within 1 mm. of those obtained in the oil thermostat for each ice point pressure. The correct ice point pressures to be associated with a series of runs from 150° to the sulphur boiling point were determined from equations based on the results obtained in the oil thermostat.

Seasoning. It was found that the ice point (or 150° point) pressure would gradually increase when the bulb was heated to the highest and cooled to the lowest temperature many times. This effect was eliminated by heating the bulb filled with nitrogen to the proper ice point pressure to the highest temperature of the complete series of runs (150° C. for the 0° to 150° series and 444.6° C. for the 150° to 444.6° C. series) for about one week. Thereafter the ice point (or 150°

point) pressure remained practically constant, sometimes increasing slightly, sometimes decreasing slightly as the measurements progressed.

Preparation for a Run. On the day before a run the mercury in the long arm of the main manometer was set about 0.1 mm. higher than the expected value, and then the injectors were used to transfer about 2 cc. of mercury from the short arm to the long arm so that the mercury in the short arm would not be in contact with the glass at the working level except during a run. The current in the external heaters of the thermostat was adjusted so that the desired temperature was approximately maintained.

On the morning of the day of a run the balance of the ratio arms and the "zero balance" of the resistance bridge were measured. The temperature of the thermostat was adjusted to within 0.003° C. of the desired International temperature and the regulation switched to the automatic regulating device.

The pumps for maintaining the vacuum in the long arms of the main and auxiliary thermometers were started. The stopcocks in the valve blocks were opened and the levels of mercury adjusted by use of the injectors until the crowns of the menisci in the short arms were 0.1 mm. below the tungsten tip. The pressure in the steel cases surrounding the thermometer bulbs was adjusted.

A run was started only after the temperature of the room and that of the air thermostat surrounding the main manometer had been satisfactorily constant for at least twelve hours; and the temperature regulation of the oil or nitrate thermostat satisfactory for one hour. A run lasted about one hour.

At the end of each day the ice point resistances of the four platinum resistance thermometers were read.

Observations. A run consisted of six sets of readings of: (1) the resistances with the commutator in the direct and reverse position of the four standard platinum resistance thermometers, and of the five short resistance thermometers in the air thermostat; (2) the temperatures of the resistance bridge, steel capillaries, scale, and auxiliary manometer; (3) the barometer, mercury levels in the auxiliary manometer and in the open manometer; and (4) the settings (average of three readings) of the micrometers in the oculars of the telescopes when the cross-hairs were on the crown and on the bottom of the mercury menisci in the long and short arms of the main manometer, the settings on the tungsten tips, and the settings on the scale divisions nearest these positions.

For four of the six sets of readings that composed a run, one experimenter made the observations (1) and a second the observations (2) to (4); for the last two sets the experimenters exchanged positions.

7. Summary

A duplicate constant volume gas thermometer for the realization of the absolute temperature scale from 0° to 450° C. is described. Methods of construction, calibration, and testing are given. The performances of the various units are outlined. The procedure used for comparison of the International Temperature Scale with the absolute scale is given.

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AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE

VII. THE THEORY OF THE CORRECTION OF THE OBSERVATIONS ON GAS THERMOMETERS FOR THE IMPERFECTIONS OF THE APPARATUS AND OF THE THERMOMETRIC FLUID

By James A. Beattie, Manson Benedict, and Joseph Kaye

TABLE OF CONTENTS

1. Introduction . . . 344
2. Reduction of Observed Mercury Heights to Standard Conditions . . . 346
3. Calculation of the Errors of Approximations . . . 348
4. Correction of the Observed Pressure of a Constant Volume Gas Thermometer for the Non-Ideality of the Apparatus
   (a) Notation and Units . . . 349
   (b) General Relation . . . 351
   (c) Gravitational Correction . . . 352
   (d) Correction for Volume and Temperature Variations . . . 353
   (e) Correction to δ_5 and δ_6 for the Departure of the Gas from a Perfect Gas . . . 354
   (f) Correction to an Integral Temperature . . . 355
   (g) Summary of Errors Introduced by the Approximations . . . 355
   (h) Other Sources of Error . . . 355
5. Theory and Performance of the Auxiliary Thermometer
   (a) Theory . . . 356
   (b) Assumptions Made in the Derivation . . . 358
   (c) Elimination of the Error Due to Assumption (4) . . . 359
   (d) Performance of the Auxiliary Thermometer . . . 359
6. Correction of the Observed Volume of a Constant Pressure Gas Thermometer for the Non-Ideality of the Apparatus
   (a) Method I . . . 360
   (b) Method II . . . 361
7. Correction of the Thermometric Coefficients and Gas Temperatures for the Imperfection of the Gas
   (a) Correction from Compressibility Data . . . 362
   (b) Correction from Joule and Joule-Thomson Coefficients . . . 365
8. Summary of Observations, Data, and Formulae for Correction of the Measurements for a Constant Volume Gas Thermometer
   (a) Quantities Measured in Each Run . . . 367
   (b) Calibration Quantities . . . 367
   (c) Properties of Materials . . . 368
   (d) Equations . . . 368
   (e) Tabulated Values . . . 369
9. Summary . . . 370

1. Introduction

Two types of gas thermometers—constant volume and constant pressure—are in general use for the realization of the absolute temperature scale. In each the experimental instrument differs from the idealized one in important respects and the real thermometric fluid differs from a perfect one.

In the idealized constant volume (or constant density) gas thermometer a definite mass N of gas is enclosed in a bulb of invariant volume V_0, the density of the gas being constant throughout the bulb. The pressures p_0, p_{100}, and p_t of the gas are measured while the bulb is thermostated at the respective temperatures 0°, 100°, t° C. The mean coefficient α_v of thermal pressure increase at constant volume of the gas from 0° to 100° C., and the Centigrade temperature t_v on the constant volume scale of the gas (corresponding to t° C.), each for the gas density corresponding to a pressure of p_0 at 0° C., are defined by means of the relations:

$$p_{100} = p_0 (1 + 100\,\alpha_v), \qquad (V = \text{constant};\ N = \text{constant}) \tag{1}$$

$$p_t = p_0 (1 + \alpha_v t_v), \qquad (V = \text{constant};\ N = \text{constant}) \tag{2}$$

where α_v has the same value in both equations. Eq. (1) may be written:

$$p_{100} V_{100} = p_0 V_0 (1 + 100\,\alpha_v), \qquad (V_{100} = V_0;\ N = \text{constant}) \tag{3}$$

$$\alpha_v = \frac{p_{100} - p_0}{100 p_0} = \frac{p_{100} V_{100} - p_0 V_0}{100\, p_0 V_0}; \qquad (V_{100} = V_0;\ N = \text{constant}) \tag{4}$$

and Eq. (2) written:

$$p_t V_t = p_0 V_0 (1 + \alpha_v t_v), \qquad (V_t = V_0;\ N = \text{constant}) \tag{5}$$

$$t_v = \frac{p_t - p_0}{\alpha_v p_0} = \frac{p_t V_t - p_0 V_0}{\alpha_v p_0 V_0}, \qquad (V_t = V_0;\ N = \text{constant}) \tag{6}$$

$$= 100 \frac{p_t - p_0}{p_{100} - p_0} = 100 \frac{p_t V_t - p_0 V_0}{p_{100} V_{100} - p_0 V_0}. \qquad (V_t = V_{100} = V_0;\ N = \text{constant}) \tag{7}$$

There are two forms of idealized constant pressure gas thermometer. In the first a definite mass N of gas is enclosed in a bulb of variable volume, the pressure being constant throughout the system and having the value p_0. The volumes V_0, V_{100}, and V_t of the bulb are measured when the bulb is thermostated at the respective temperatures 0°, 100°, t° C., the pressure being brought to the value p_0 at each temperature by adjustment of the volume of the bulb. The mean coefficient α_p of thermal dilation at constant pressure of the gas from 0° to 100° C., and the Centigrade temperature t_p on the constant pressure scale of the gas (corresponding to t° C.), each for the gas pressure p_0, are defined by means of the relations:

$$V_{100} = V_0 (1 + 100\,\alpha_p), \qquad (p = \text{constant};\ N = \text{constant}) \tag{8}$$

$$V_t = V_0 (1 + \alpha_p t_p), \qquad (p = \text{constant};\ N = \text{constant}) \tag{9}$$

where α_p has the same value in both equations. Eq. (8) may be written:

$$p_{100} V_{100} = p_0 V_0 (1 + 100\,\alpha_p), \qquad (p_{100} = p_0;\ N = \text{constant}) \tag{10}$$

$$\alpha_p = \frac{V_{100} - V_0}{100 V_0} = \frac{p_{100} V_{100} - p_0 V_0}{100 p_0 V_0}; \qquad (p_{100} = p_0;\ N = \text{constant}) \tag{11}$$

and Eq. (9) written:

$$p_t V_t = p_0 V_0 (1 + \alpha_p t_p), \qquad (p_t = p_0;\ N = \text{constant}) \tag{12}$$

$$t_p = \frac{V_t - V_0}{\alpha_p V_0} = \frac{p_t V_t - p_0 V_0}{\alpha_p p_0 V_0}, \qquad (p_t = p_0;\ N = \text{constant}) \tag{13}$$

$$= 100 \frac{V_t - V_0}{V_{100} - V_0} = 100 \frac{p_t V_t - p_0 V_0}{p_{100} V_{100} - p_0 V_0}. \qquad (p_t = p_{100} = p_0;\ N = \text{constant}) \tag{14}$$

In the second form of idealized constant pressure thermometer a definite mass N of gas is enclosed in a bulb of invariant volume V_b connected by a tube of negligible volume to a pipette of variable volume v which is kept at a constant temperature (say 0° C.), the pressure being constant throughout the system and having the value p_0. The method of operation is the same as that described in the preceding paragraph except that the pressure is adjusted to p_0 at each bulb temperature by adjustment of the volume of gas in the pipette. Let v_0, v_{100}, and v_t be the gas volumes in the pipette (at 0° C.) when the bulb temperatures are, respectively, 0°, 100°, t° C. Then:

$$V_b + v_0 = \frac{V_b}{1+100\alpha_p} + v_{100}, \qquad (p = \text{constant};\ N = \text{constant}) \tag{15}$$

$$V_b + v_0 = \frac{V_b}{1+\alpha_p t_p} + v_t, \qquad (p = \text{constant};\ N = \text{constant}) \tag{16}$$

where α_p has the same value in both equations. Thus:

$$\alpha_p = \frac{1}{100}\,\frac{v_{100}-v_0}{V_b-(v_{100}-v_0)}, \qquad (p = \text{constant};\ N = \text{constant}) \tag{17}$$

$$t_p = \frac{1}{\alpha_p}\,\frac{v_t-v_0}{V_b-(v_t-v_0)}. \qquad (p = \text{constant};\ N = \text{constant}) \tag{18}$$

Let D_0, D_{100}, and D_t be the gas densities in the bulb at the respective temperatures 0°, 100°, t° C. Then

$$N = D_0\,(V_b + v_0).$$

The number of moles of gas in the bulb at 100° and t° C. are, respectively:

$$N_{b100} = D_0\,(V_b + v_0) - D_0\,v_{100},$$

$$N_{bt} = D_0\,(V_b + v_0) - D_0\,v_t;$$

and the densities of the gas *in the bulb* at 100° and t° C. are, respectively:

$$D_{100} = \frac{N_{b100}}{V_b} = D_0\,\frac{V_b-(v_{100}-v_0)}{V_b},$$

$$D_t = \frac{N_{bt}}{V_b} = D_0\,\frac{V_b-(v_t-v_0)}{V_b}.$$

Whence:

$$D_0 = D_{100}\,(1 + 100\,\alpha_p), \qquad (p = \text{constant}) \tag{19}$$

$$D_0 = D_t\,(1 + \alpha_p\,t_p), \qquad (p = \text{constant}) \tag{20}$$

where α_p has the same value in both equations; and:

$$\alpha_p = \frac{D_0-D_{100}}{100D_{100}}, \qquad (p = \text{constant}) \tag{21}$$

$$t_p = \frac{D_0-D_t}{\alpha_p D_t}. \qquad (p = \text{constant}) \tag{22}$$

In all of the Eqs. (8) to (22) each of the quantities α_p and t_p has the same numerical value for a given pressure p_0 of a given gas. The practical constant pressure gas thermometer corresponds to the second type of idealized instrument described. Eqs. (8) to (14) may however be used, the gas in the pipette being considered as part of the dead space. The method of making the correction for this effect is presented in a later section.

In the experimental constant volume or constant pressure gas thermometer the pressure is measured on a manometer (usually mercury) which is outside of the thermostat surrounding the thermometer bulb and is connected to the bulb by a fine capillary. Thus a part of the system is at a

temperature different from that of the bulb (or those of the bulb and pipette); furthermore the walls of the system are strained because of changes in pressure and temperature, and the system is in a gravitational field.

The observed quantities must be corrected for: (1) the imperfections of the manometer system; and (2) the deviation of the practical from the idealized thermometer system. When pressures or volumes so corrected are substituted into the relations given above, there result values of α_v, t_v, α_p, and t_p which depend on the kind of gas used and on the density or pressure of the gas at 0° C., and not on the imperfections of the practical thermometer system.

The general thermodynamic theory of real and perfect gases[1] gives the result that for any gas:

$$\lim_{p_0 \to 0} \alpha_v = \lim_{p_0 \to 0} \alpha_p = \alpha = \frac{1}{T_0}, \tag{23}$$

and

$$\lim_{p_0 \to 0} t_v = \lim_{p_0 \to 0} t_p = t. \tag{24}$$

In these equations α is the thermometric coefficient, α_v or α_p, of an ideal gas:

$$\alpha = \frac{p_{100}V_{100} - p_0V_0}{100\, p_0V_0}. \qquad (p_{100} = p_0 \text{ or } V_{100} = V_0;\ N = \text{constant})$$

$$= \frac{RT_{100} - RT_0}{100\, RT_0} = \frac{1}{T_0}, \tag{25}$$

and is independent of density; T_0 is the Kelvin temperature of the ice point; and t is thermodynamic temperature on the Centigrade scale, the corresponding Kelvin temperature T being

$$T = t + T_0. \tag{26}$$

The extrapolation to zero ice-point pressure indicated in Eqs. (23) and (24) may be accomplished: (1) by determination of the value of the quantity for several different ice-point pressures and extrapolation to zero pressure by graphical or analytic methods; (2) by determination of the value of the quantity for one or more ice-point pressures and correction for the deviation of the properties of the real from those of the ideal gas by means of (a) compressibility data on the gas or (b) values of the Joule (for α_v and t_v) or Joule-Thomson (for α_p and t_p) coefficients for the gas. Since Joule coefficients are difficult to measure, the values of α_v and t_v may be corrected to zero ice-point pressure from combined measurements of compressibility and of Joule-Thomson coefficients. Method (1) requires only gas thermometric measurements; method (2) requires in addition auxiliary thermodynamic data on the gas used.

The present paper is concerned with the computation of Kelvin temperatures from the observations made with constant volume and constant pressure gas thermometers, and in particular the corrections necessitated by the imperfections of the manometer system, the thermometer system, and the thermometric fluid. In the preceding paper[2] are given a description of a duplicate constant volume gas thermometer and auxiliary equipment, methods of calibration and testing, performance of the apparatus, and the method of taking observations.

2. Reduction of Observed Mercury Heights to Standard Conditions

The corrections to be applied to the observations made on a mercury manometer with a comparator, having two telescopes which can be rigidly clamped to the vertical bar, and a scale are: (1) the scale corrections, and (2) the mercury corrections.

The uncorrected difference H in elevation between the mercury surface in the long arm and in the short arm of the manometer is

[1] J. A. Beattie, Phys. Rev., **36,** 132–145 (1930); *Temperature*, pp. 74–88, Reinhold Publ. Corp., New York, 1941.

[2] J. A. Beattie, D. D. Jacobus, J. M. Gaines, Jr., M. Benedict, and B. E. Blaisdell, Proc. Am. Acad. Arts Sci., **74,** 327–342 (1941).

$$H = D_1 - D_2 + m\,(M_1 - M_2 - S_1 + S_2); \tag{27}$$

and the heights h_1 and h_2 of the mercury menisci in the long and short arms of the manometer, respectively, are:

$$h_1 = m\,(M_1 - N_1), \tag{28}$$

$$h_2 = m\,(M_2 - N_2), \tag{29}$$

where:

$M_1[M_2]$ = average reading of micrometer head of upper [lower] telescope when the cross-hair of the ocular is set on the crown of the mercury meniscus in the long [short] arm of the manometer.

$N_1[N_2]$ = average reading on bottom of meniscus.

$S_1[S_2]$ = average reading on scale division $D_1[D_2]$.

$D_1[D_2]$ = scale division nearest cross-hair of upper [lower] telescope when set on $M_1[M_2]$.

m = number of units on the scale per one complete turn of the micrometer head; it is the same for both telescopes.

The scale corrections to be applied to the height H are: (1) the ruling error of the scale, (2) the thermal extension of the scale, and (3) the extension of the scale under its weight. The following relation is without appreciable error for a scale hung from its upper end:

$$p'' = H + \varepsilon_1 - \varepsilon_2 + \alpha_s H(t_s - t_{sn}) + \frac{\rho_s g_l}{2E_s} H(H + 2D_2)\,, \tag{30}$$

where:

p'' = pressure (mm.) corrected for scale corrections.

ε_1 = scale correction (mm.) for the position $H + D_2$.

ε_2 = scale correction (mm.) for the position D_2.

α_s = mean coefficient of linear thermal expansion (°C.$^{-1}$) of the scale material from t_{sn} to t_s.

t_s = mean temperature (°C.) of the scale.

t_{sn} = temperature (°C.) at which scale was calibrated.

ρ_s = density (gm./mm.^{3}) of the scale material.

g_l = gravity (cm./sec.^{2}) at the laboratory.

E_s = Young's modulus (dynes/mm.^{2}) of the scale material.

Any other consistent set of units may be used in Eq. (30). The mercury corrections to be applied to p'' are: (1) the difference between the capillary depression of mercury in the long arm and in the short arm of the manometer, (2) the thermal dilation and the compressibility of mercury, and (3) the effect of gravity. The relation is:

$$p' = (p'' + \delta_1 - \delta_2)\frac{V(0, 1)\,g_l}{V(t, p)\,g_n}, \tag{31}$$

$$V(t, p) = V(0, 1)\left[1 + \alpha_{Hg}\,t_{Hg}\right]\left[1 - \beta_{Hg}\frac{p' - 760}{2 \times 760}\right], \tag{32}$$

where:

p' = corrected pressure (mm.) at crown of mercury meniscus in the short arm of the manometer.

δ_1 = capillary depression (mm.) of mercury in long arm of manometer.

δ_2 = capillary depression in short arm.

g_n = standard gravity, 980.665 cm./sec.^{2}

$V\,(0, 1)$ = mean specific volume of mercury in a column 760 mm. high at 0° C.

$V(t, p)$ = mean specific volume of mercury in a column p' mm. high at a mean temperature of t_{Hg}.

t_{Hg} = mean temperature (°C.) of mercury column.

α_{Hg} = mean coefficient of thermal dilation (°C.$^{-1}$) of mercury from 0° to t_{Hg} °C.

β_{Hg} = mean coefficient of cubical compressibility (atm.$^{-1}$) of mercury from 0 to 3 atm. at mean room temperature.

Let

$$F = \frac{g_l}{g_n} \frac{1}{1 + \alpha_{Hg} t_{Hg}}; \tag{33}$$

then Eq. (31) may be written without appreciable error:

$$p' = \left[p'' + \delta_1 - \delta_2 \right] \left[1 + \beta_{Hg} \frac{HF - 760}{1520} \right] F. \tag{34}$$

Substitution of the value of p'' from Eq. (30) and simplification gives without appreciable error:

$$p' = [H + \delta_1 - \delta_2 + \delta_3] F, \tag{35}$$

$$\delta_3 = \varepsilon_1 - \varepsilon_2 + \alpha_s H(t_s - t_{sn}) + \frac{\rho_s g_l}{2E_s} H(H + 2D_2) + \beta_{Hg} H \frac{HF - 760}{1520}. \tag{36}$$

In Eq. (36) the value of F for the mean room temperature may be used without appreciable error. This approximation together with the others made in deriving the above expressions introduces for a height H of 2000 mm. an error less than 1×10^{-4} mm. for a scale of invar, brass, or glass correct at 0° or 20° C. when used from a room temperature of 10° to 30° C.

For an invar scale, for which $t_{sn} = 20°$ C., $\alpha_s = 1.5 \times 10^{-6°}$ C.$^{-1}$, $\rho_s = 8.0 \times 10^{-3}$ grams/mm.^{3}, $g_l = 980.400$ cm./sec.^{2}, $E_s = 1.45 \times 10^{10}$ dynes/mm.^{2}, used to measure the height of a mercury column in millimeters at a mean room temperature of 27° C., at which $\beta_{Hg} = 4.0 \times 10^{-6}$ atm.$^{-1}$ and $F = 0.995$, we obtain:

$$\delta_3 = \varepsilon_1 - \varepsilon_2 + 1.5 \times 10^{-6} H (t_s - 20) + 2.89 \times 10^{-9} H (H - 692 + 0.19 D_2). \tag{37}$$

For a manometer used in gas thermometric measurements D_2 is constant. Thus ε_2 and the diameter of the short arm at D_2 are constant; and ε_1 and the diameter of the long arm at $H + D_2$ are functions of H. For the use of Eq. (35) we may tabulate F as a function of t_{Hg}, δ_1 as a function of h_1 and H, δ_2 as a function of h_2, and δ_3 as a function of t_s and H.

3. Calculation of the Errors of Approximations

In the derivation of the equations in the succeeding sections higher order terms in certain expressions have been dropped. The value of each such term has been computed for the following cases:

Case I. A nitrogen gas thermometer with a bulb of Jena 16^{III} glass or of vitreous silica loaded to a pressure of 1000 mm. at 0° C. and used from 0° to 450° C. The ratio of the dead space to the total volume is taken to be 0.005 with 5% of the dead space in the region of large thermal gradient, 20% in the connecting capillaries at room temperature, and 75% in the short arm of the manometer. The vertical height of the part of the system at the temperature of the bulb is taken to be 250 mm., that part in the region of large thermal gradient 500 mm., and that part at room temperature — 500 mm.

Case II. A helium gas thermometer with a bulb of Jena 16^{III} or of Jena 1565^{III} glass loaded to a pressure of 1000 mm. at 0° C., and used from 100° to − 200° C.; and one loaded to a pressure of 1000 mm. at − 183° C. and used from − 183° to − 260° C. The dead spaces and heights are taken to be the same as in Case I.

4. Correction of the Observed Pressure of a Constant Volume Gas Thermometer for the Non-Ideality of the Apparatus

The object of this section is to derive an equation for correction of the observed pressure p' at the mercury surface in the short arm of the manometer to the pressure p at the center of the bulb which

would have been found if: (1) the gravitational field were absent; (2) the volume of the system were constant; and (3) all of the gas were at the temperature of the bulb.

A sketch of a constant volume gas thermometer is given in Fig. 1. AS is the main thermometer system, A_aS_a the auxiliary thermometer system.

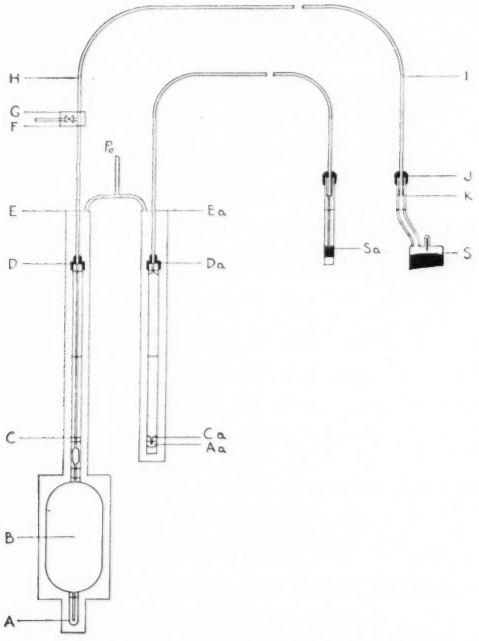

FIG. 1. Main gas thermometer system AS and auxiliary gas thermometer system A_aS_a.

(a) *Notation and Units*

In the use of the relations derived in this and the following sections any consistent set of units may be used. A suggested set is:

pressure in standard mm. of mercury,
volume in ml.,
area in ml./mm.,
length in mm.,
mass in moles for gases and grams for condensed systems,
temperature (T) in degrees Kelvin,
temperature (t) in degrees Centigrade on the International Scale,
the gas constant $R = 62360$ ml.-mm./°K.-mole.

The following symbols are used:

General. p = pressure.
V = volume.
T = Kelvin temperature.
t = Centigrade temperature on the International Scale.
N = number of moles of gas.
M = molecular weight of the gas.
A, B, C = parameters, functions of temperature, in the equation of state of a gas:

$$p\frac{V}{N} = A + Bp + Cp^2, \tag{38}$$

$$A \equiv RT. \tag{39}$$

δ_{Hg} = standard density of mercury (13.5955 gm./ml.).

Practical Gas Thermometer. x = distance along the axis of the thermometric system measured from A, the bottom of the bulb.

$a = a(x)$ = area of the section of the system at x normal to the axis.

$\pi = \pi(x)$ = pressure of the gas at x.

p' = pressure at the crown of the mercury meniscus in the short arm of the manometer.

$\phi = \phi(x)$ = hydrostatic head function at x defined by the relation $\pi = p'(1 + \phi)$.

p_e = pressure in the case surrounding the thermometer bulb.

$\delta_g = \delta_g(x)$ = density (moles/ml.) of the gas at x.

$T = T(x)$ = Kelvin temperature at x.

$\theta = \theta(x)$ = angle between an arrow in the axis of the thermometer pointing in the direction of increasing x and one pointing vertically upward.

l = vertical height, the algebraic sign being the same as that of $\cos\theta$. l_b is the vertical distance from the *center of the thermometer bulb* to the beginning of the dead space.

h_2 = height of mercury meniscus in the short arm of the manometer.

h_3 = distance from crown of meniscus to index mark in short arm of manometer.

a_m = area of short arm of manometer at the index mark.

Subscript a denotes that the quantity applies to the auxiliary gas thermometer.

Subscript b denotes the bulb.

Subscript d denotes the dead space taken as a whole.

Subscript i denotes the i-th dead space: $i = 1$ is the region of large thermal gradient contiguous to the bulb, $i = 2, 3, 4, \ldots$ are the successive contiguous dead space regions, $i = m$ is the dead space in the short arm of the manometer.

Subscript n denotes the value of a quantity at the standard condition of calibration. We took:

V_{bn} = volume of bulb at 0° C. and 1 atm. pressure inside and outside.

V_{in} = volume of i-th dead space ($i = 1, 2, \ldots m - 1$) at 27° C. and 1 atm. pressure.

V_{mn} = dead space volume in short arm of manometer above a horizontal plane through the index mark at 27° C. and 1 atm. pressure increased by a quantity Δ, which is somewhat less than the smallest expected volume below the plane through the index mark.

V_{ban} = volume of bulb of auxiliary thermometer at 27° C. and 1 atm. pressure.

V_{dan} = volume of total dead space of auxiliary thermometer at 27° C. and 1 atm. pressure.

Subscript r denotes the nominal (integral) International temperature of the thermostat for a run. Thus if $t_b = 150.0018°$, $t_r = 150°$ C.

Idealized Gas Thermometer. p = pressure. It is equal to p' plus the corrections for the deviation of the practical from the idealized instrument.

V = volume. It is equal to the volume of the practical instrument under the standard conditions of calibration, i. e., $V_{bn} + \sum_1^m {}_i V_{in}$.

Properties of Materials. α_b = mean coefficient of thermal dilation $(1/V_{bn})(\Delta V_b/\Delta t)°$ C.$^{-1}$, of the material of the bulb from $t_{bn}°$ to $t_r°$ C. at 1 atmosphere pressure; it is a function of temperature.

α_b' = true coefficient of thermal dilation $(1/V_{bn})(dV_b/dt)°$ C.$^{-1}$, of the material of the bulb at $t_r°$ C. and 1 atmosphere pressure; it is a function of temperature.

$\frac{\beta_b}{760}$ = mean coefficient of cubical compressibility, $-(1/V_{bn})(\Delta V_b/\Delta p)$ mm.$^{-1}$, of the material of the bulb from 0 to 3 atm. at $t_r°$ C.; it is a function of temperature.

γ_b = mean dilation, $\Delta V_b/(p_b - p_e)$ ml./mm., of the bulb at t_r° C. produced by difference between internal and external pressure; it is a function of temperature.

α_i = mean coefficient of thermal dilation (°C.$^{-1}$) of the material surrounding the i-th dead space ($i = 2, 3, 4, \ldots m$) from t_{i_0}° to t_i° C.

V_0 = covolume of mercury meniscus, i. e., gas volume below a horizontal plane through the crown of the meniscus.

(b) General Relation

The number of moles of gas in the practical gas thermometer, constant throughout all runs of the same ice-point pressure, is

$$N = \int_A^S \frac{\pi a dx}{A + B\pi + C\pi^2}, \tag{40}$$

$$= p' \int_A^S \frac{a\,(1+\phi)\,dx}{A + B\,(1+\phi)\,p' + C\,(1+\phi)^2\,p'^2} \equiv p' \int_A^S \psi dx. \tag{41}$$

In an equivalent idealized gas thermometer at the temperature T_b

$$N = \frac{pV}{A_b + B_b p + C_b\,p^2}. \tag{42}$$

Equating these two expressions for N and solving for the corrected pressure p, we obtain:

$$p = \frac{A_b p'}{V}\left\{1 + \frac{B_b p'}{V}\int_A^S \psi dx + \frac{C_b p p'}{V}\int_A^S \psi dx + \left[\frac{B_b^2 p'^2}{V^2} + \frac{2B_b C_b p p'^2}{V^2}\right]\left(\int_A^S \psi dx\right)^2 + \frac{B_b^3 p'^3}{V^3}\left(\int_A^S \psi dx\right)^3 + \ldots\right\}\int_A^S \psi dx. \tag{43}$$

The expansion of ψ is

$$\psi = \frac{a}{A}\left\{1 - \frac{B}{A}p' + \phi - \frac{C}{A}p'^2 + \frac{B^2}{A^2}p'^2 - \frac{2B\phi}{A}p' + \frac{2BC}{A^2}p'^3 - \frac{B^3}{A^3}p'^3 + \ldots\right\}. \tag{44}$$

Substitution of this value of ψ into Eq. (43) and simplification gives

$$p = \frac{A_b p'}{V}\left\{\int_A^S \frac{a}{A}dx + \frac{B_b p'}{V}\left(\int_A^S \frac{a}{A}dx\right)^2 - p'\int_A^S \frac{Ba}{A^2}dx + \int_A^S \frac{\phi a}{A}dx\right\} + \frac{A_b p'}{V}\left\{\left[\frac{C_b p p'}{V}\left(\int_A^S \frac{a}{A}dx\right)^2 - p'^2\int_A^S \frac{Ca}{A^2}dx\right] + \left[p'^2\int_A^S \frac{B^2 a}{A^3}dx + \frac{B_b^2 p'^2}{V^2}\left(\int_A^S \frac{a}{A}dx\right)^3 - \frac{2B_b p'^2}{V}\int_A^S \frac{Ba}{A^2}dx\int_A^S \frac{a}{A}dx\right]\right\} + \ldots \tag{45}$$

The expression enclosed in the second set of braces consists of two groups of paired terms of opposite sign, each group enclosed in a bracket. These terms cancel almost completely for the bulb (A to C of Fig. 1) of the thermometer which contains practically all of the gas, and partly cancel for the gas in the dead space. If we drop these terms, substract p' from each side of the equation, add and subtract $\frac{p'}{V}\int_A^S adx$ to the right hand side of the equation, replace A by RT, and correct p to an integral bulb temperature, we obtain

$$p - p' = \delta_4 + \delta_5 + \delta_6 + \delta_7 + \delta_8, \tag{46}$$

where:

$$\delta_4 = \frac{p'T_b}{V}\int_A^S \frac{\phi a}{T}\,dx = \text{gravitational correction.} \tag{47}$$

$$\delta_5 = \frac{p'}{V}\left[\int_A^S a\,dx - V\right] = \text{correction for variation of volume of the system on the assumption that the gas is ideal.} \tag{48}$$

$$\delta_6 = \frac{p'}{V}\left[T_b\int_A^S \frac{a}{T}\,dx - \int_A^S a\,dx\right] = \text{correction for variation of temperature of the system on the assumption that the gas is ideal.} \tag{49}$$

$$\delta_7 = \frac{p'^2 T_b}{RV}\left[\frac{B_b}{V}\left(\int_A^S \frac{a}{T}\,dx\right)^2 - \int_A^S \frac{Ba}{T^2}\,dx\right] = \text{correction to } (\delta_5 + \delta_6) \text{ for the imperfection of the gas.} \tag{50}$$

$$\delta_8 = p_0\,\alpha_v\,(t_r - t_b) = \text{correction to an integral temperature, } t_r. \tag{51}$$

The maximum error of Eq. (45) for either Case is 0.1×10^{-4} mm. of mercury; the maximum error of Eq. (46) is -6×10^{-4} mm. for Case I (at 444.6° C.) and less than -1×10^{-4} mm. for Case II (at − 260° C.).

(c) Gravitational Correction

The correction for the effect of the gravitational field is

$$\delta_4 = \frac{p'T_b}{V}\int_A^S \frac{\phi a}{T}\,dx. \tag{52}$$

Now

$$\int_\pi^{p'} d\pi = -\int_x^S \frac{M\delta_g}{\delta_{Hg}}\cos\theta\,dx. \tag{53}$$

Integration yields

$$\pi = p'(1 + \phi), \tag{54}$$

where

$$\phi = \frac{M}{\delta_{Hg}}\int_x^S \frac{\pi}{p'}\,\frac{\cos\theta\,dx}{A + B\pi + C\pi^2}. \tag{55}$$

Let:

$$\frac{\pi}{p'} = 1, \tag{56}$$

$$B = C = 0, \tag{57}$$

in the integrand of Eq. (55). Then

$$\phi = \frac{M}{R\delta_{Hg}}\int_x^S \frac{\cos\theta}{T}\,dx. \tag{58}$$

The assumptions (56) and (57) are justified since the maximum value of ϕ is 100×10^{-6} and its value is much smaller than this for the bulb which contains practically all of the gas.

Substitution of the value of ϕ from Eq. (58) into Eq. (52) gives:

$$\delta_4 = \frac{p'T_b}{V}\int_A^S \left(\frac{M}{R\delta_{Hg}}\int_x^S \frac{\cos\theta}{T}\,dx\right)\frac{a}{T}\,dx, \tag{59}$$

$$= 1.1795 \times 10^{-6} M \frac{p' T_b}{V} \int_A^S \left(\int_x^S \frac{\cos\theta}{T} dx \right) \frac{a}{T} dx, \tag{60}$$

$$= 1.1795 \times 10^{-6} M p' \left\{ \frac{V_b}{V} \left[\frac{l_b}{T_b} + \int_C^D \frac{\cos\theta}{T} dx + \sum_2^m{}^i \frac{l_i}{T_i} \right] + \frac{T_b}{V} \int_C^D \left(\int_x^S \frac{\cos\theta}{T} dx \right) \frac{a}{T} dx \right.$$

$$\left. + \sum_2^m{}^i \left[\frac{V_i}{V} \frac{T_b}{T_i} \left(\frac{l_i}{2T_i} + \sum_{i+1}^m{}^j \frac{l_j}{T_j} \right) \right] \right\}; \tag{61}$$

where CD is the region of large thermal gradient (see Fig. 1). Since the volume of the bulb is large compared to the volume of the dead space, Eq. (61) may be written:

$$\delta_4 = 1.1795 \times 10^{-6} M \frac{p' V_b}{V} \left[\frac{l_b}{T_b} + \int_C^D \frac{\cos\theta}{T} dx + \sum_2^m{}^i \frac{l_i}{T_i} \right]. \tag{62}$$

In a later section it will be shown that

$$\int_C^D \frac{\cos\theta}{T} dx = \frac{l_1}{T_1}, \tag{63}$$

where $1/T_1$ is evaluated by the use of the auxiliary thermometer $A_a S_a$. Thus:

$$\delta_4 = 1.1795 \times 10^{-6} M \frac{p' V_b}{V} \left[\frac{l_b}{T_b} + \sum_1^m{}^i \frac{l_i}{T_i} \right]. \tag{64}$$

The lengths l_b and l_i depend on temperature and the method of suspension of the thermometer bulb, and l_m depends on h_3.

The three approximations made are: (1) $\pi/p' = 1$, $B = C = 0$ in the evaluation of ϕ; (2) the dropping of certain terms of Eq. (61); and (3) the evaluation of δ_4 for the region CD by Eq. (63). The first two introduce a maximum error of -4×10^{-4} mm. of mercury for Case I and less than $+1 \times 10^{-4}$ mm. for Case II. The error introduced by the third assumption depends on the design of the apparatus. For our gas thermometers the error was $+3 \times 10^{-4}$ mm. of mercury when the bulb was at 444.6° C. and $+1 \times 10^{-4}$ mm. when at 180° C. for the run at 600 mm. ice-point loading.

(*d*) *Correction for Volume and Temperature Variations*

The correction for the variation of the volume of the system with temperature and pressure, and that for the variation of temperature are:

$$\delta_5 = \frac{p'}{V} \left[\int_A^S a dx - V \right], \tag{65}$$

$$\delta_6 = \frac{p'}{V} \left[T_b \int_A^S \frac{a}{T} dx - \int_A^S a dx \right]. \tag{66}$$

Integration yields:

$$\delta_5 = \frac{p'}{V} \left[\left(V_b - V_{bn} \right) + \left(\int_C^D a dx - V_{1n} \right) + \sum_2^m{}^i \left(V_i - V_{in} \right) \right], \tag{67}$$

$$\delta_6 = \frac{p'}{V} \left[\left(T_b \int_C^D \frac{a}{T} dx - \int_C^D a dx \right) + \sum_2^m{}^i V_i \left(\frac{T_b}{T_i} - 1 \right) \right]. \tag{68}$$

For the region of large thermal gradient CD the sum:

$$\left(\delta_5 + \delta_6\right)_{CD} = \frac{p'}{V}\left(T_b \int_C^D \frac{a}{T}\, dx - V_{1n}\right), \tag{69}$$

$$= \frac{p'}{V} V_{1n}\left(\frac{T_b}{T_1} - 1\right), \tag{70}$$

where V_{1n} is the volume of the region of large thermal gradient *at standard conditions* and $1/T_1$ is evaluated by use of the auxiliary thermometer. The derivation of Eq. (70) is given in a later section.

Thus:

$$\delta_5 = \frac{p'}{V}\left[(V_b - V_{bn}) + \sum_2^m{}_i (V_i - V_{in})\right], \tag{71}$$

$$\delta_6 = \frac{p'}{V}\left[V_{1n}\left(\frac{T_b}{T_1} - 1\right) + \sum_2^m{}_i V_i\left(\frac{T_b}{T_i} - 1\right)\right]. \tag{72}$$

We may write with negligible error:

$$V_b - V_{bn} = V_{bn}\left[\alpha_b\,(t_r - t_{bn}) + \alpha_b'\,(t_b - t_r) - \frac{\beta_b}{760}\,(p' - 760)\right] + \gamma_b\,(p' - p_e), \tag{73}$$

$$V_i - V_{in} = V_{in}\,\alpha_i\,(t_i - t_{in}), \qquad (i = 2, 3, 4, \ldots m - 1) \tag{74}$$

$$V_m - V_{mn} = V_{mn}\,\alpha_m\,(t_m - t_{mn}) + \Delta V_m, \tag{75}$$

$$\Delta V_m = a_m\, h_3 + V_c - \Delta. \tag{76}$$

The quantity ΔV_m is the increase in the volume below a plane through the index mark in the short arm of the manometer from the value Δ. For manometer tubes 20 mm. in diameter we took Δ to be 0.1 ml. Then $(a_m\, h_3 + V_c)$ is always larger than Δ so that ΔV_m is always positive; and the value of δ_5 is much less than if we had considered ΔV_m to be the total quantity $(a_m\, h_3 + V_c)$.

The assumption that V_i is independent of pressure introduces a negligible error. The only other approximation made is the evaluation of $(\delta_5 + \delta_6)$ for the region CD by Eq. (70). The error introduced depends on the design of the apparatus. For our gas thermometers the error was $+ 25 \times 10^{-4}$ mm. of mercury when the bulb was at 444.6° C. and $+ 3 \times 10^{-4}$ mm. when at 180° C. for the run at 600 mm. ice-point loading.

(c) Correction to δ_5 and δ_6 for the Departure of the Gas from a Perfect Gas

The correction δ_7:

$$\delta_7 = \frac{p'^2 T_b}{RV}\left[\frac{B_b}{V}\left(\int_A^S \frac{a}{T}\, dx\right)^2 - \int_A^S \frac{Ba}{T^2}\, dx\right] \tag{77}$$

gives on integration

$$\delta_7 = \frac{p'^2 T_b}{RV}\left[\frac{B_b}{V}\left(\frac{V_b}{T_b} + \int_C^D \frac{a}{T}\, dx + \sum_2^m{}_i \frac{V_i}{T_i}\right)^2 - \left(\frac{V_b B_b}{T_b^2} + \int_C^D \frac{Ba}{T^2}\, dx + \sum_2^m{}_i \frac{V_i B_i}{T_i^2}\right)\right]. \tag{78}$$

The first integral of Eq. (78) can be evaluated as

$$\int_C^D \frac{a}{T}\, dx = \frac{V_{1n}}{T_1}, \tag{79}$$

and the second approximated as

$$\int_C^D \frac{Ba}{T^2}\, dx = \frac{B_1}{T_1}\int_C^D \frac{a}{T}\, dx = \frac{B_1 V_{1n}}{T_1^2}, \tag{80}$$

by use of the indications of the auxiliary thermometer, where B_1 is the value of the second virial coefficient of the gas at T_1.

Carrying out the indicated operations and dropping the squares and products of small terms, we obtain from Eq. (78):

$$\delta_7 = \frac{p'^2}{RV}\left[\frac{B_b V_b}{V}\left(\frac{V_b - V}{T_b} + 2\sum_1^m{}_i \frac{V_i}{T_i}\right) - T_b \sum_1^m{}_i \frac{B_i V_i}{T_i^2}\right], \tag{81}$$

where V_i signifies V_{1n} for $i = 1$. If we put the ratio $V_b/V = 1$ the error is of opposite sign and of the same order as that made in the terms dropped in Eq. (78) when either error is at all appreciable; also T_r can be written for T_b with no perceptible error.

Hence Eq. (81) may be written:

$$\delta_7 = \frac{p'^2}{RV}\left[B_r\left(\frac{V_b - V}{T_r} + 2\sum_1^m{}_i \frac{V_i}{T_i}\right) - T_r \sum_1^m{}_i \frac{B_i V_i}{T_i^2}\right], \tag{82}$$

where B_r is the value of B at T_r.

The approximations made are: (1) the dropping of certain terms of Eq. (78) and placing $V_b/V = 1$ in Eq. (81); and (2) the evaluation of δ_7 for the region CD by Eqs. (79) and (80). The maximum error of the first is $+ 2 \times 10^{-4}$ mm. of mercury for Case I and less than $- 1 \times 10^{-4}$ mm. for Case II. The error introduced by the second depends on the design of the apparatus. For our gas thermometers the error was $+ 1 \times 10^{-4}$ mm. of mercury when the bulb was at 444.6° C. and 0×10^{-4} mm. when at 180° C. for the 600 mm. ice-point loading.

(*f*) *Correction to an Integral Temperature*

The temperature t_b of the thermostat surrounding the bulb will in general differ from the nominal (integral) temperature t_r of the run by several thousandths of a degree. The correction for this effect is

$$\delta_8 = p_0 \alpha_v (t_r - t_b), \tag{83}$$

where p_0 is the ice-point pressure for the run and α_v is the approximate mean coefficient of thermal pressure increase at constant volume from 0° to 100° C. of the gas for an ice-point pressure p_0.

(*g*) *Summary of Errors Introduced by the Approximations*

The maximum errors of all approximations made in deriving the preceding equations are $- 8 \times 10^{-4}$ mm. of mercury for Case I and $- 1 \times 10^{-4}$ mm. for Case II. In addition there is the error of the evaluation of the corrections for the region CD of large thermal gradient by use of the indications of the auxiliary thermometer. We determined this error experimentally for our gas thermometer and found it to be $+ 29 \times 10^{-4}$ mm. for a bulb temperature of 444.6° C. and $+ 4 \times 10^{-4}$ mm. for a bulb temperature of 180° C. for the run with an ice-point pressure of 600 mm. The error is almost proportional to the ice-point pressure for any one temperature. It will be noticed that this error decreases rapidly with decreasing temperature difference from room temperature.

(*h*) *Other Sources of Error*

Other sources of error that should be considered in the design and operation of a gas thermometer are:

(1) Calibration errors.
(2) Errors in the assumed properties of materials, especially in the coefficient of thermal expansion of the material of the bulb.
(3) Hysteresis in the properties of materials, especially in the effect of pressure and temperature on the volume of the bulb.
(4) Ageing effects, especially the effect of time on the length of the scale.
(5) Passage of gas through the walls of the thermometer system.
(6) Adsorption of gas on the walls of the thermometer bulb.
(7) Thermal diffusion pressure.

The design of a constant volume thermometer with a view to eliminating the effects of these sources of error to a greater or less extent and the methods of testing the achievement of this result are given in the preceding paper.[2]

The thermal diffusion pressure can be estimated from an equation[3] which has been tested for helium from room temperature to liquid helium temperatures. For nitrogen in a tube of 0.70 mm. bore, one temperature being 450° and the other 27° C., the computed effect is 5×10^{-4} mm. of mercury for a pressure of 871 mm. ($p_0 = 333$ mm.), and 2.5×10^{-4} mm. for a pressure of 1569 mm. ($p_0 = 600$ mm.).

5. Theory and Performance of the Auxiliary Thermometer

(a) *Theory*

In the preceding section there occurred three expressions:

$$\delta_{4CD} = 1.1795 \times 10^{-6} M \frac{p' V_b}{V} \int_C^D \frac{\cos\theta}{T}\, dx, \tag{84}$$

$$\left(\delta_5 + \delta_6\right)_{CD} = \frac{p'}{V}\left(T_b \int_C^D \frac{a}{T}\, dx - V_{1n}\right), \tag{85}$$

$$\delta_{7CD} = \frac{p'^2}{RV}\left(2B_r \int_C^D \frac{a}{T}\, dx - T_r \int_C^D \frac{Ba}{T^2}\, dx\right), \tag{86}$$

for the region of large thermal gradient CD, Fig. 1. This gradient may be quite large so that the device of segregation of CD into several regions essentially isothermal and evaluation of the integrals as sums of terms would require many terms and thus a prohibitive amount of labor. The three integrals:

$$\int_C^D \frac{a}{T}\, dx, \qquad \int_C^D \frac{\cos\theta}{T}\, dx, \qquad \int_C^D \frac{Ba}{T^2}\, dx,$$

can be evaluated, the first two quite exactly, and the last approximately, by use of the auxiliary gas thermometer $A_a S_a$, Fig. 1.

For the nitrogen thermometer of Case I at 450° C., $\delta_{4CD} = 0.1$ mm., $(\delta_5 + \delta_6)_{CD} = 0.4$ mm., and $\delta_{7CD} = 0.003 - 0.0015 = 0.0015$ mm.

A theory of the auxiliary thermometer has been outlined by Henning.[4]

The relations derived in the preceding sections may be applied to the auxiliary thermometer. Some further approximations can be made without the introduction of serious error. In the computation of p_a' from Eq. (35) we may write:

$$\delta_{1a} - \delta_{2a} = \delta_a, \tag{87}$$

$$\delta_{3a} = 0, \tag{88}$$

where δ_a is the mean capillary depression correction (a constant value) applied to all observations. Thus

$$p_a' = (H_a + \delta_a) F_a. \tag{89}$$

In the application of Eq. (41) to the auxiliary thermometer we may write

$$B_a = C_a = \phi_a = 0; \tag{90}$$

whence:

$$N_a = p_a' \int_{A_a}^{S_a} \frac{a_a}{A_a}\, dx_a, \tag{91}$$

[3] S. Weber, W. H. Keesom, and G. Schmidt, Kamerlingh Onnes Lab., Univ. of Leiden, Comm. No. **246a,** 1–16.

[4] F. Henning, *Temperaturmessung*, p. 46, F. Vieweg und Sohn, Braunschweig, 1915.

$$= \frac{p_a'}{R} \int_{A_a}^{S_a} \frac{a_a}{T_a} dx_a. \tag{92}$$

Let:

$$\int_{A_a}^{D_a} a_a dx_a = V_{ba}, \tag{93}$$

$$\int_{D_a}^{S_a} a_a dx_a = \sum_1^m{}_i V_{ia} = V_{da}, \tag{94}$$

$$r_{an} = \frac{V_{dan}}{V_{ban} + V_{dan}} \equiv \frac{V_{dan}}{V_{an}}. \tag{95}$$

The volume of the bulb is assumed to depend only on temperature; and that of the dead space is assumed to be constant. The coefficient of thermal expansion of the material of the bulb is the same as that of the capillary CD of the main thermometer.

In order to calibrate the auxiliary thermometer for the evaluation of the integrals of Eqs. (84) to (86), the bulb is thermostated at the standard temperature T_{ban}, and the pressure p'_{an} and mean temperature T_{dan} of the dead space determined. From Eq. (92):

$$\frac{N_a R}{V_{an}} = \frac{p'_{an}}{V_{an}} \left(\frac{V_{ban}}{T_{ban}} + \frac{V_{dan}}{T_{dan}} \right) = p'_{an} \left(\frac{1 - r_{an}}{T_{ban}} + \frac{r_{an}}{T_{dan}} \right) \equiv \Phi_{an}, \tag{96}$$

where Φ_{an} is a constant for all runs made with a given loading of the auxiliary thermometer.

When the auxiliary thermometer is used in a gas thermometer run, the pressure p_a' and the mean temperature T_{da} of the dead space are determined. Then

$$\frac{N_a R}{V_{an}} = \frac{p_a'}{V_{an}} \left(\int_{A_a}^{D_a} \frac{a_a}{T_a} dx_a + \frac{V_{dan}}{T_{da}} \right). \tag{97}$$

From Eq. (97) and the calibration data of Eq. (96), we obtain

$$\int_{A_a}^{D_a} \frac{a_a}{T_a} dx_a = \frac{\Phi_{an} V_{an}}{p_a'} - \frac{V_{dan}}{T_{da}} \tag{98}$$

Let the capillary CD of the main thermometer and the bulb $A_a D_a$ of the auxiliary thermometer fulfill the conditions that in every horizontal plane:

$$T(x) = T_a(x_a), \tag{99}$$

$$a(x) = k\, a_a(x_a), \tag{100}$$

where k is independent of x and of temperature. Then:

$$\frac{\int_C^D \frac{a}{T} dx}{\int_C^D a dx} = \frac{\int_{A_a}^{D_a} \frac{a_a}{T_a} dx_a}{\int_{A_a}^{D_a} a_a dx_a}, \tag{101}$$

or

$$\int_C^D \frac{a}{T} dx = \frac{V_1}{V_{ba}} \int_{A_a}^{D_a} \frac{a_a}{T_a} dx_a, \tag{102}$$

$$= \frac{V_{1n}}{V_{ban}} \int_{A_a}^{D_a} \frac{a_a}{T_a} dx_a, \tag{103}$$

since the coefficients of thermal dilation of CD and A_aD_a are the same. Substitution from Eq. (98) into Eq. (103) gives:

$$\int_C^D \frac{a}{T} dx = \left(\frac{\Phi_{an} V_{an}}{p_a'} - \frac{V_{dan}}{T_{da}} \right) \frac{V_{1n}}{V_{ban}}. \tag{104}$$

Let

$$\frac{1}{T_1} \equiv \frac{1}{V_{ban}} \left(\frac{\Phi_{an} V_{an}}{p_a'} - \frac{V_{dan}}{T_{da}} \right) = \frac{\dfrac{\Phi_{an}}{p_a'} - \dfrac{r_{an}}{T_{da}}}{1 - r_{an}}. \tag{105}$$

The quantity $1/T_1$ is the reciprocal temperature along A_aD_a, hence by hypothesis that along CD, averaged with respect to area. Then

$$\int_C^D \frac{a}{T} dx = \frac{V_{1n}}{T_1}. \tag{106}$$

If the bore of CD is uniform,

$$\int_C^D \frac{\cos \theta}{T} dx = \frac{l_1}{T_1}. \tag{107}$$

Finally let B/T be constant for the gas in CD and have its value B_1/T_1, at T_1. Then

$$\int_C^D \frac{Ba}{T^2} dx = \frac{B_1 V_{1n}}{T_1^2}. \tag{108}$$

The integrals given at the beginning of the section can now be evaluated as:

$$\mathfrak{d}_{4CD} = 1.1795 \times 10^{-6} M \frac{p' V_b}{V} \frac{l_1}{T_1}, \tag{109}$$

$$\left(\mathfrak{d}_5 + \mathfrak{d}_6 \right)_{CD} = \frac{p'}{V} V_{1n} \left(\frac{T_b}{T_1} - 1 \right), \tag{110}$$

$$\mathfrak{d}_{7CD} = \frac{p'^2}{RV} \left(2B_r \frac{V_{1n}}{T_1} - T_r \frac{B_1 V_{1n}}{T_1^2} \right). \tag{111}$$

(b) *Assumptions Made in the Derivation*

The assumptions made in the above derivation are:

(1) For the auxiliary manometer: $\mathfrak{d}_1 - \mathfrak{d}_2 = \mathfrak{d}_a$ (a constant) and $\mathfrak{d}_3 = 0$.
(2) For the gas in the auxiliary thermometer: $B_a = C_a = \phi_a = 0$.
(3) The volume of the bulb of the auxiliary thermometer depends only on temperature; the dead space volume is constant.
(4) For the capillary CD and the tube A_aD_a: $a(x) = ka_a(x_a)$ where k is independent of x (or x_a) and of temperature.
(5) For CD and A_aD_a: $T(x) = T_a(x_a)$ in each horizontal plane.
(6) For CD: the area a is constant and $\cos \theta = 1$.
(7) For the gas in CD: B/T is constant and has the value B_1/T_1.

Assumptions (1) to (3) affect the computed value of $1/T_1$. If we take maximum values[5] for the effects of these assumptions, the errors in T_1 are less than 0.6, 0.2, and 0.1° C. for thermostat temperatures of 444.6°, 100°, and 0° C., respectively, when the auxiliary thermometer is filled with nitrogen to a pressure of 1000 mm. at 0° C.; and the errors are less than 0.1° C. for all thermostat temperatures from 100° to − 260° C. for a thermometer filled with helium to 1000 mm. at 0° C. The error is proportional to the ice-point pressure of the thermometer.

(c) *Elimination of the Error Due to Assumption (4)*

The error introduced into Eqs. (109) to (111) by the assumption that k, Eq. (100), is independent of x can be eliminated for any one thermostat temperature if the areas and corresponding temperatures of CD and A_aD_a are known as functions of the respective coordinates x and x_a. At the same time the proper lengths of CD to be associated with the short capillary sections at the ends of A_aD_a are determined. Computation has shown that if the error is eliminated for the thermostat temperature farthest from room temperature it will also be eliminated for all other thermostat temperatures.

From a plot of the indications of thermocouples (placed along CD) against x, we can determine the temperature at the middle of each of the m one-centimeter intervals of CD, each assumed to be isothermal. The most important integral of Eqs. (84) to (86) to be evaluated in order to obtain Eqs. (109) to (111) could then be computed as the sum:

$$T_r \int_C^D \frac{a}{T}\, dx = T_r \sum_1^m{}_j \frac{V_j}{T_j} \tag{112}$$

where V_j and T_j are the volume and Kelvin temperature of the j-th one-centimeter interval of CD and T_r is the nominal temperature of the thermostat. If assumption (4) is fulfilled:

$$T_r \sum_1^m{}_j \frac{V_j}{T_j} = T_r \frac{V_{1n}}{V_{ban}} \sum_1^m{}_j \frac{V_{aj}}{T_{aj}} \tag{113}$$

where

$$T_j = T_{aj},\ V_{1n} = \sum_1^m{}_j V_{nj},\ V_{ban} = \sum_1^m{}_j V_{anj} \tag{114}$$

and V_{aj} is the volume of the j-th one-centimeter section of the bulb of the auxiliary thermometer. The assumptions made are: (1) $T_j = T_{aj}$, and (2) the coefficients of thermal dilation of V_j and V_{aj} are the same ($j = 1, 2, \ldots m$). By slight adjustment of the length of the top or bottom section of CD or both, we can cause Eq. (113) to be completely satisfied. This new length of CD is then taken as the value of l_1 at T_r from which l_{1n} can be computed.

We measured the temperature along CD of our two gas thermometers by means of seven thermocouples for a thermostat temperature of 444.6° C. and one of 180° C. The values of the lengths of the end sections of CD that satisfied Eq. (113) for 444.6° C. also satisfied it for 180° C.

The region below CD is assigned to the bulb of the main thermometer, the region above to the dead space 2.

(d) *Performance of the Auxiliary Thermometer*

With the elimination of the error due to assumption (4) we have left the error in the computed value of $1/T_1$ due to assumptions (1) to (3) and the errors due to assumptions (5) to (7). The size of these errors were determined for our gas thermometer by the determination of the value of δ_{4CD}, $(\delta_5 + \delta_6)_{CD}$, and δ_{7CD} from Eqs. (109), (110), and (111), where $1/T_1$ was evaluated from the auxiliary thermometer by Eq. (105); and from Eqs. (84), (85), and (86), the integrals being evaluated as sums of 45 terms, each for a one-centimeter section of CD. When t_r was 444.6 C. and the ice-point pressure in the main thermometer was 600 mm. the errors in δ_{4CD}, $(\delta_5 + \delta_6)_{CD}$, and δ_{7CD} were 3×10^{-4}, 25×10^{-4}, and 1×10^{-4} mm. of mercury, respectively, a total of 0.003 mm., which is within the probable accuracy of the thermocouple method. When t_r was 180° C., these errors were 1×10^{-4} mm., $3 \times$

[5] The computations were made for $V_{da}/V_{ba} = 0.1$, $A_aD_a = 500$ mm., error of assumption (1) = 0.1 mm. in p'_{an} and p_a', variation in $t_{da} = \pm 5°$ C., $p_a' = 2$ atm., $p_{ca} - p_a' = 1.5$ atm.

10^{-4} mm., and 0×10^{-4} mm., respectively, a total of about 0.0005 mm. The errors fall rapidly with decreasing temperature difference from room temperature.

6. Correction of the Observed Volume of a Constant Pressure Gas Thermometer for the Non-Ideality of the Apparatus

The method given in a previous section is directly applicable to the constant pressure gas thermometer. Two procedures are possible:

(1) The idealized thermometer is taken to be one in which all of the gas is at the bulb temperature. Eqs. (11) and (13) are to be used for computing α_p and t_p. The pipettes are treated as part of the dead space.

(2) The idealized thermometer is taken to be one with a bulb at the thermostat temperature and a pipette at some fixed temperature, say 0° C. Eqs. (17) and (18) are to be used for computing α_p and t_p. The pipettes are now not a part of the dead space.

Fig. 1 may serve as an illustration of a constant pressure gas thermometer if the pipette is imagined as being inserted between H and I. The bulb is AC and the rest of the system including the pipette is CS.

(a) *Method I*

Let V be the (variable) volume of the bulb at T_b. Application of Eqs. (41) and (42) gives:

$$\frac{p_0 V}{A_b + B_b p_0 + C_b p_0^2} = p' \int_A^S \frac{a\,(1+\phi)\,dx}{A + B\,(1+\phi)\,p' + C\,(1+\phi)^2\,p'^2}. \tag{115}$$

Solving for V and substituting from Eq. (44), we obtain:

$$V = \frac{A_b p'}{p_0}\left\{\int_A^S \frac{a}{A}\,dx + \frac{B_b p_0}{A_b}\int_A^S \frac{a}{A}\,dx - p'\int_A^S \frac{Ba}{A^2}\,dx + \int_A^S \frac{\phi a}{A}\,dx\right\} + \frac{A_b p'}{p_0}\left\{\left[\frac{C_b p_0^2}{A_b}\int_A^S \frac{a}{A}\,dx - p'^2\int_A^S \frac{Ca}{A^2}\,dx\right] + \left[p'^2\int_A^S \frac{B^2 a}{A^3}\,dx - \frac{B_b p_0 p'}{A_b}\int_A^S \frac{Ba}{A^2}\,dx\right]\right\} + \ldots . \tag{116}$$

The paired terms in the second brace are dropped. Let

$$V' = V_{bn} + \sum_1^m {}_i V_{in} + V_{Hg}, \tag{117}$$

where V_{Hg} is the volume of mercury run out of the pipette. Then

$$V - V' = \delta_4 + \delta_{5.1} + \delta_{5.2} + \delta_6 + \delta_7 + \delta_8, \tag{118}$$

where:

$$\delta_4 = \frac{p' T_b}{p_0}\int_A^S \frac{\phi a}{T}\,dx = \text{gravitational correction.} \tag{119}$$

$$\delta_{5.1} = \frac{p'}{p_0}\left[\int_A^S a\,dx - V'\right] = \text{correction for variation of volume of the system on the assumption that the gas is ideal.} \tag{120}$$

$$\delta_{5.2} = \frac{p'}{p_0} V'\left(1 - \frac{p_0}{p'}\right) = \text{correction for deviation of } p' \text{ from } p_0 \text{ on the assumption that the gas is ideal.} \tag{121}$$

$$\delta_6 = \frac{p'}{p_0}\left[T_b\int_A^S \frac{a}{T}\,dx - \int_A^S a\,dx\right] = \text{correction for variation in temperature of the system on the assumption that the gas is ideal.} \tag{122}$$

$$\delta_7 = \frac{p'^2}{Rp_0}\left[\frac{B_b p_0}{p'}\int_A^S \frac{a}{T}\,dx - T_b\int_A^S \frac{Ba}{T^2}\,dx\right] = \text{correction to } (\delta_{5.1} + \delta_{5.2} + \delta_6) \text{ for the imperfection of the gas.} \tag{123}$$

$\delta_8 = V_0\alpha_p\,(t_r - t_b)$ = correction to an integral temperature, t_r. The quantity V_0 is the ice-point volume of the run. (124)

The corrected volumes, V, are to be used in Eqs. (11) and (13) for computing α_p and t_p. The pressure p_0 is constant for all runs with the same ice-point pressure. It may be taken equal to p' for the run at 0° C.

(b) Method II

In the idealized thermometer let V_b be the (constant) volume (AC, Fig. 1) of the bulb at T_b and v the (variable) volume (CS, Fig. 1) of the pipette at T_0. Application of Eqs. (41) and (42) gives:

$$\frac{p_0 V_b}{A_b + B_b p_0 + C_b p_0^2} + \frac{p_0 v}{A_0 + B_0 p_0 + C_0 p_0^2} = p'\int_A^S \frac{a\,(1+\phi)\,dx}{A + B\,(1+\phi)p' + C\,(1+\phi)^2\,p'^2}. \tag{125}$$

Solving for v and substituting from Eq. (44), we obtain:

$$\begin{aligned} v = \frac{A_0 p'}{p_0}\Bigg\{&\int_A^S \frac{a}{A}\,dx - \frac{V_b p_0}{A_b p'} + \frac{B_0 p_0}{A_0}\int_A^S \frac{a}{A}\,dx - p'\int_A^S \frac{Ba}{A^2}\,dx - \frac{V_b p_0^2}{A_b p'}\left(\frac{B_0}{A_0} - \frac{B_b}{A_b}\right) + \int_A^S \frac{\phi a}{A}\,dx\Bigg\} \\ &+ \frac{A_0 p'}{p_0}\Bigg\{\left[\frac{C_0 p_0^2}{A_0}\int_A^S \frac{a}{A}\,dx - p'^2\int_A^S \frac{Ca}{A^2}\,dx - \frac{V_b p_0^3}{A_b p'}\left(\frac{C_0}{A_0} - \frac{C_b}{A_b}\right)\right] \\ &+ \left[p'^2\int_A^S \frac{B^2 a}{A^3}\,dx - \frac{B_0 p_0 p'}{A_0}\int_A^S \frac{Ba}{A^2}\,dx - \frac{V_b p_0^3}{A_b p'}\frac{B_b}{A_b}\left(\frac{B_b}{A_b} - \frac{B_0}{A_0}\right)\right]\Bigg\} + \ldots . \end{aligned} \tag{126}$$

The paired terms in the second brace are dropped. Let

$$v' = \sum_1^m {}_i\, v_{in} + v_{Hg}, \tag{127}$$

where v_{Hg} is the volume of mercury run out of the pipette. Then

$$v - v' = \delta_4 + \delta_{5.1} + \delta_{5.2} + \delta_6 + \delta_7 + \delta_8, \tag{128}$$

where:

$$\delta_4 = \frac{p'}{p_0}\frac{T_0}{}\int_A^S \frac{\phi a}{T}\,dx. \tag{129}$$

$$\delta_{5.1} = \frac{p'}{p_0}\left[\frac{T_0}{T_b}\left(\int_A^C a dx - V_b\right) + \left(\int_C^S a dx - v'\right)\right]. \tag{130}$$

$$\delta_{5.2} = \frac{p'}{p_0}\left(\frac{V_b\,T_0}{T_b} + v'\right)\left(1 - \frac{p_0}{p'}\right). \tag{131}$$

$$\delta_6 = \frac{p'}{p_0}\left[T_0\int_A^S \frac{a}{T}\,dx - \frac{T_0}{T_b}\int_A^C a dx - \int_C^S a dx\right]. \tag{132}$$

$$\delta_7 = \frac{p'^2}{Rp_0}\left[\frac{B_0 p_0}{p'}\int_A^S \frac{a}{T}dx - T_0\int_A^S \frac{Ba}{T^2}\,dx - V_b\frac{T_0}{T_b}\frac{p_0^2}{p'^2}\left(\frac{B_0}{T_0} - \frac{B_b}{T_b}\right)\right]. \tag{133}$$

$\delta_8 = \dfrac{V_b\alpha_p T_0^2}{T_b^2}(t_r - t_b)$. The quantity V_b is the volume of the bulb at standard conditions. (134)

The corrected volumes, v, are to be used in Eqs. (17) and (18) for the computation of α_p and t_p.

The further reduction of Eqs. (119) to (124) or Eq. (129) to (134) can be carried out in a manner similar to that used in a preceding section for the constant volume gas thermometer.

7. Correction of the Thermometric Coefficients and Gas Temperatures for the Imperfection of the Gas

When the pressures or volumes corrected for the deviations of the experimental thermometer from the corresponding idealized one are substituted into the proper one of the Eqs. (1) to (22), there result values of α_v, t_v, α_p, or t_p which depend upon the gas used and the ice-point pressure of the run. The computation of the corresponding values of these quantities for zero pressure, see Eqs. (23) to (25), is usually made from compressibility data on the gas employed or from measured Joule-Thomson and Joule coefficients supplemented if necessary by compressibility data.

There is a rather extensive literature on this subject.[6]

(a) *Correction from Compressibility Data*

The isothermal compressibility data for a constant mass of a gas can be fitted in the low pressure region by an equation of the type:

$$pV = A + Bp + Cp^2; \tag{135}$$

or one of the type:

$$pV = A\left(1 + \frac{B}{V} + \frac{C'}{V^2}\right), \tag{136}$$

where A, B, C, C' are functions only of temperature for a given gas. The quantities A and B should have the same numerical values in Eq. (136) as in Eq. (135), and

$$C' = AC + B^2; \qquad C = \frac{C' - B^2}{A}. \tag{137}$$

It can be shown [1] that A must obey the relations

$$\frac{A}{A_0} = \frac{T}{T_0} = 1 + \alpha t, \tag{138}$$

and if V is the volume of one mole of gas

$$A = RT, \tag{139}$$

where R is the universal gas constant, T is Kelvin temperature, t the corresponding absolute Centigrade temperature, T_0 the Kelvin temperature of the ice-point, and α the thermometric coefficient of an ideal gas.

When Eqs. (135) and (136) are applied to isothermal compressibility data, say by the method of least squares, the relations between B, C, and C' given above will not be satisfied exactly. Eq. (136) gives a better representation of the measurements than Eq. (135) when the same pressure range is considered.

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For the purposes of writing some of the following equations in more condensed form, let us define:

$$\Delta(x) \equiv \begin{vmatrix} 1 & 1 & 1 \\ x_0 T_0 & x_{100} T_{100} & x_t T \\ T_0 & T_{100} & T \end{vmatrix},$$

$$= (x_{100} T_{100} - x_0 T_0)\, t - (x_t T - x_0 T_0)\, 100, \tag{140}$$

$$= (x_{100} - x_0)\, T_{100} t - (x_t - x_0)\, 100\, T, \tag{141}$$

where T is Kelvin temperature, $t = T - T_0$, and the subscripts 0 and 100 refer to 0° and 100° C. When the symbol $\Delta\,(x)_v$ [or $\Delta\,(x)_p$] is used, t is to be replaced by the gas temperature t_v, [or t_p], as defined in Eqs. (6) or (13); and T by $(T_0 + t_v)$, [or $(T_0 + t_p)$]. Thus:

$$\Delta(B) = (B_{100} - B_0)\, T_{100} t - (B_t - B_0)\, 100 T,$$

$$\Delta(B)_v = (B_{100} - B_0)\, T_{100} t_v - (B_t - B_0)\, 100\, (T_0 + t_v),$$

$$\Delta(B/T) = (B_{100} - B_0)\, t - (B_t - B_0)\, 100,$$

etc. The values of the virial coefficients B, C, C' at any temperature should be independent of the value assigned to the temperature. Actually, since A_t is computed as $A_0\, T/T_0$, the values of B, C, and C' do depend to some extent on the value assigned to T, which should be on the Kelvin scale.

Constant Volume Gas Thermometer. For the constant volume gas thermometer the mass of gas is constant and V is constant and has the value V_0. The following relations will be found useful in the treatment of the data:

$$pV_0 = A + B\frac{A}{A_0} p_0 + \left[C + \frac{B}{A}(B - B_0)\right]\frac{A^2}{A_0^2} p_0^2, \tag{142}$$

$$= A\left\{1 + B\frac{p_0}{A_0} + \left[C' - B\,B_0\right]\frac{p_0^2}{A_0^2}\right\}, \tag{143}$$

$$\frac{p}{p_0} = \frac{A}{A_0}\left\{1 + (B - B_0)\frac{p_0}{A_0} + \left[(CA - C_0 A_0) + (B - B_0)^2\right]\frac{p_0^2}{A_0^2}\right\}, \tag{144}$$

$$= \frac{A}{A_0}\left\{1 + (B - B_0)\frac{p_0}{A_0} + \left[(C' - C_0') - 2B_0\,(B - B_0)\right]\frac{p_0^2}{A_0^2}\right\}, \tag{145}$$

$$\frac{p_0}{p} = \frac{A_0}{A}\left\{1 - (B - B_0)\frac{p_0}{A_0} - (CA - C_0 A_0)\frac{p_0^2}{A_0^2}\right\}, \tag{146}$$

$$= \frac{A_0}{A}\left\{1 - (B - B_0)\frac{p_0}{A_0} - \left[(C' - C_0') - (B^2 - B_0^2)\right]\frac{p_0^2}{A_0^2}\right\}. \tag{147}$$

Substitution of the values of pV_0 from Eqs. (142) and (143) into Eq. (4) yields:

$$\alpha = \alpha_v - \frac{1 + 100\alpha}{100}\frac{B_{100} - B_0}{A_0} p_0 \left\{1 + \left[\frac{C_{100}\,(1 + 100\alpha) - C_0}{B_{100} - B_0} + \frac{B_{100} - B_0}{A_0}\right] p_0\right\}, \tag{148}$$

$$= \alpha_v - \frac{1 + 100\alpha}{100}\frac{B_{100} - B_0}{A_0} p_0 \left\{1 + \left[\frac{C'_{100} - C_0'}{B_{100} - B_0} - 2B_0\right]\frac{p_0}{A_0}\right\}. \tag{149}$$

Substitution of the values of pV_0 into Eq. (7) yields:

$$t = t_v + \frac{\Delta(B)}{100 A_0} p_0 \left\{1 + \left[\frac{100 A_0}{T_0}\frac{\Delta(CT)}{\Delta(B)} + 100\frac{\Delta(B^2)}{\Delta(B)} - (B_{100} + B_0)\, T_{100} + 2B_0 T_0\right]\frac{p_0}{100 A_0}\right\}, \tag{150}$$

$$= t_v + \frac{\Delta(B)}{100 A_0} p_0 \left\{1 + \left[100\frac{\Delta(C')}{\Delta(B)} - (B_{100} + B_0)\, T_{100} + 2B_0 T_0\right]\frac{p_0}{100 A_0}\right\}. \tag{151}$$

Eqs. (148) to (151) may be written:

$$\alpha = \alpha_v - \frac{1 + 100\alpha_v}{100}\frac{B_{100} - B_0}{A_0} p_0 \left\{1 + \frac{C_{100}(1 + 100\alpha_v) - C_0}{B_{100} - B_0} p_0\right\}, \tag{148a}$$

$$= \alpha_v - \frac{1 + 100\alpha_v}{100}\frac{B_{100} - B_0}{A_0} p_0 \left\{1 + \left[\frac{C'_{100} - C_0'}{B_{100} - B_0} - (B_{100} + B_0)\right]\frac{p_0}{A_0}\right\}, \tag{149a}$$

$$t = t_v + \frac{\Delta(B)_v}{100A_0} p_0 \left\{1 + \left[\frac{A_0}{T_0}\frac{\Delta(CT)_v}{\Delta(B)_v} + \frac{\Delta(B^2)_v}{\Delta(B)_v} - (B_t + B_0)\right]\frac{p_0}{A_0}\right\}, \tag{150a}$$

$$= t_v + \frac{\Delta(B)_v}{100A_0} p_0 \left\{1 + \left[\frac{\Delta(C')_v}{\Delta(B)_v} - (B_t + B_0)\right]\frac{p_0}{A_0}\right\}. \tag{151a}$$

Constant Pressure Gas Thermometer. For the constant pressure gas thermometer the mass of gas is constant and p is constant and has the value p_0. The following relations are useful:

$$p_0V = A + B\,p_0 + C\,p_0^2, \tag{152}$$

$$= A\left[1 + B\frac{p_0}{A} + (C' - B^2)\frac{p_0^2}{A^2}\right], \tag{153}$$

$$\frac{V}{V_0} = \frac{A}{A_0}\left\{1 + \left(\frac{B}{A} - \frac{B_0}{A_0}\right)p_0 + \left[\left(\frac{C}{A} - \frac{C_0}{A_0}\right) - \frac{B_0}{A_0}\left(\frac{B}{A} - \frac{B_0}{A_0}\right)\right]p_0^2\right\}, \tag{154}$$

$$= \frac{A}{A_0}\left\{1 + \left(\frac{B}{A} - \frac{B_0}{A_0}\right)p_0 + \left[\left(\frac{C'}{A^2} - \frac{C_0'}{A_0^2}\right) - \left(\frac{B^2}{A^2} + \frac{B\,B_0}{A\,A_0} - \frac{2B_0^2}{A_0^2}\right)\right]p_0^2\right\}, \tag{155}$$

$$\frac{V_0}{V} = \frac{A_0}{A}\left\{1 - \left(\frac{B}{A} - \frac{B_0}{A_0}\right)p_0 - \left[\left(\frac{C}{A} - \frac{C_0}{A_0}\right) - \frac{B}{A}\left(\frac{B}{A} - \frac{B_0}{A_0}\right)\right]p_0^2\right\}, \tag{156}$$

$$= \frac{A_0}{A}\left\{1 - \left(\frac{B}{A} - \frac{B_0}{A_0}\right)p_0 - \left[\left(\frac{C'}{A^2} - \frac{C_0'}{A_0^2}\right) - \left(\frac{2B^2}{A^2} - \frac{B\,B_0}{A\,A_0} - \frac{B_0^2}{A_0^2}\right)\right]p_0^2\right\}. \tag{157}$$

Substitution of the values of p_0V from Eqs. (152) and (153) into Eq. (11) gives:

$$\alpha = \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha)}{100A_0} p_0 \left\{1 + \left[\frac{C_{100} - C_0(1 + 100\alpha)}{B_{100} - B_0(1 + 100\alpha)} - \frac{B_0}{A_0}\right]p_0\right\}, \tag{158}$$

$$= \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha)}{100A_0} p_0 \left\{1 + \left[\frac{C'_{100} - C_0'(1 + 100\alpha)^2}{B_{100} - B_0(1 + 100\alpha)} - B_{100} - 2B_0(1 + 100\alpha)\right]\frac{p_0}{A_0(1 + 100\alpha)}\right\}. \tag{159}$$

Substitution of the values of p_0V into Eq. (14) gives:

$$t = t_p + \frac{T_0\Delta(B/T)}{100A_0} p_0 \left\{1 + \left[100A_0\frac{\Delta(C/T)}{\Delta(B/T)} - T_0(B_{100} - B_0)\right]\frac{p_0}{100A_0}\right\}. \tag{160}$$

$$= t_p + \frac{T_0\Delta(B/T)}{100A_0} p_0 \left\{1 + \left[100\frac{\Delta(C'/T^2)}{\Delta(B/T)} - 100\frac{\Delta(B^2/T^2)}{\Delta(B/T)} - (B_{100} - B_0)\right]\frac{T_0p_0}{100A_0}\right\}. \tag{161}$$

Eqs. (158) to (161) may be written:

$$\alpha = \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha_p)}{100A_0} p_0 \left\{1 + \frac{C_{100} - C_0(1 + 100\alpha_p)}{B_{100} - B_0(1 + 100\alpha_p)} p_0\right\}, \tag{158a}$$

$$= \alpha_p - \frac{B_{100} - B_0(1 + 100\alpha_p)}{100A_0} p_0 \left\{1 + \left[\frac{C'_{100} - C_0'(1 + 100\alpha_p)^2}{B_{100} - B_0(1 + 100\alpha_p)} - B_{100} - B_0(1 + 100\alpha_p)\right]\frac{p_0}{A_0(1 + 100\alpha_p)}\right\}, \tag{159a}$$

$$t = t_p + \frac{T_0\Delta(B/T)_p}{100A_0}\, p_0 \left\{1 + \frac{\Delta(C/T)_p}{\Delta(B/T)_p}\, p_0\right\}, \tag{160a}$$

$$= t_p + \frac{T_0\Delta(B/T)_p}{100A_0}\, p_0 \left\{1 + \left[\frac{\Delta(C'/T^2)_p}{\Delta(B/T)_p} - \frac{\Delta(B^2/T^2)_p}{\Delta(B/T)_p}\right]\frac{T_0 p_0}{A_0}\right\}. \tag{161a}$$

(b) Correction from Joule and Joule-Thomson Coefficients

Let η be the Joule coefficient and μ the Joule-Thomson coefficient of a gas:

$$\eta = -\left(\frac{\partial T}{\partial V}\right)_U = \frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}, \tag{162}$$

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{(\partial H/\partial p)_T}{(\partial H/\partial T)_p}; \tag{163}$$

and let $C_v = (\partial U/\partial T)_V$ and $C_p = (\partial H/\partial T)_p$ be the heat capacities at constant volume and constant pressure, respectively. Then λ,

$$\lambda \equiv \eta C_v, \tag{164}$$

can be used to correct α_v and t_v for the deviation of the thermometric gas from an ideal gas; and σ,

$$\sigma \equiv \mu C_p, \tag{165}$$

can be used to correct α_p and t_p. Since accurate experimental determinations of the Joule coefficient η have not been made, the quantity λ is computed from σ and compressibility data by use of the thermodynamic equation:

$$\lambda = -\sigma\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial (pV)}{\partial V}\right)_T. \tag{166}$$

The partial derivatives in Eq. (166) may be evaluated from the equation of state (136).

Constant Volume Gas Thermometer. Let

$$\lambda \equiv \eta C_v = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \equiv -\left[\frac{\partial (p/T)}{\partial (1/T)}\right]_V. \tag{167}$$

Thus

$$d\left(\frac{p}{T}\right) = -\lambda d\left(\frac{1}{T}\right); \qquad (V = \text{constant}) \tag{168}$$

and integration from 0° to 100° C. at constant volume gives:

$$\frac{p_{100}}{T_{100}} - \frac{p_0}{T_0} = -\int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right), \qquad (V = V_0 = \text{constant}) \tag{169}$$

the integral being evaluated along the constant volume (or density) curve to which α_v refers (the density of the gas at p_0 and T_0). Substitution of the value of P_{100} obtained from Eq. (169) into Eq. (4) and use of Eq. (25) give:

$$\alpha = \alpha_v + \frac{1 + 100\alpha}{100\,\alpha p_0} \int_{T_0}^{T_{100}} \lambda d\left(\frac{1}{T}\right), \tag{170}$$

where p_0 and λ are to be expressed in the same units. In the first approximation the quantity α on the right hand side of the equation can be replaced by α_v or by the approximate value $\alpha = 0.003661$, T_0 taken to be 273.16, and λ expressed as a function of $(T_0 + t_v)$.

Integration of Eq. (168) from 0° to t° C. gives:

$$\frac{p_t}{T} - \frac{p_0}{T_0} = -\int_{T_0}^{T} \lambda d\left(\frac{1}{T}\right). \qquad (V = V_0 = \text{constant}) \tag{171}$$

Substitution of the value of p_t from Eq. (171) and p_{100} from Eq. (169) into Eq. (7) gives:

$$t = t_v + \frac{T_0}{100 p_0}\left[100T\int_{T_0}^{T}\lambda d\left(\frac{1}{T}\right) - t_v\, T_{100}\int_{T_0}^{T_{100}}\lambda d\left(\frac{1}{T}\right)\right] \tag{172}$$

In the first approximation T can be replaced by $(T_0 + t_v)$, T_0 taken to be 273.16, and λ expressed as a function of $(T_0 + t_v)$.

It will be noted that λ can be computed from the equation of state parameters through Eq. (167). Thus from Eq. (136) we find:

$$\lambda = \frac{AT}{V^2}\left[\left(\frac{dB}{dT}\right) + \frac{1}{V}\left(\frac{dC'}{dT}\right)\right], \tag{173}$$

$$= -\frac{R}{V^2}\left[\frac{dB}{d\,(1/T)} + \frac{1}{V}\frac{dC'}{d\,(1/T)}\right]. \tag{174}$$

Constant Pressure Gas Thermometer. Let

$$\sigma \equiv \mu C_p = -\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P - V \equiv -\left[\frac{\partial\,(V/T)}{\partial\,(1/T)}\right]_P. \tag{175}$$

Thus

$$d\left(\frac{V}{T}\right) = -\sigma d\left(\frac{1}{T}\right); \qquad (p = \text{constant}) \tag{176}$$

and integration from 0° to 100° C. at constant pressure gives:

$$\frac{V_{100}}{T_{100}} - \frac{V_0}{T_0} = -\int_{T_0}^{T_{100}}\sigma d\left(\frac{1}{T}\right), \qquad (p = p_0 = \text{constant}) \tag{177}$$

the integral being evaluated along the constant pressure curve, p_0, to which α_p refers. Substitution of the value of V_{100} from Eq. (177) into Eq. (11) and use of the relation (25) give:

$$\alpha = \alpha_p + \frac{1 + 100\alpha}{100\alpha\, V_0}\int_{T_0}^{T_{100}}\sigma d\left(\frac{1}{T}\right). \tag{178}$$

The quantity V_0 may be computed from T_0 and p_0 by Eq. (135), and is to be expressed in the same units as σ. The same approximation may be made as for Eq. (170).

Integration of Eq. (176) from 0° to t° C. gives:

$$\frac{V_t}{T} - \frac{V_0}{T_0} = -\int_{T_0}^{T}\sigma d\left(\frac{1}{T}\right). \qquad (p = p_0 \text{ constant}) \tag{179}$$

Substitution of the value of V_t from Eq. (179) and V_{100} from Eq. (177) into Eq. (14) gives:

$$t = t_p + \frac{T_0}{100 V_0}\left[100T\int_{T_0}^{T}\sigma d\left(\frac{1}{T}\right) - t_p\, T_{100}\int_{T_0}^{T_{100}}\sigma d\left(\frac{1}{T}\right)\right]. \tag{180}$$

the same approximations may be made as for Eq. (172).

From Eq. (175) and the equation of state (135) we find:

$$\sigma = \left(T\frac{dB}{dT} - B\right) + \left(T\frac{dC}{dT} - C\right)p, \tag{181}$$

$$= -\left(\frac{d\,(B/T)}{d\,(1/T)} + \frac{d\,(C/T)}{d\,(1/T)}\,p\right). \tag{182}$$

At the present time no accurate experimentally determined Joule coefficients are available[7] and very few Joule-Thomson coefficients. The most accurate measurements of the latter type are those of Roebuck and his associates. Yet his values of λ for nitrogen computed from his measured μ coefficients, heat capacities, and compressibility data by Eq. (166) are obviously in disagreement with all of the compressibility data in the temperature range 0° to 100° C. since he finds from his computations[8] that the values of the Kelvin Temperature of the ice-point calculated from our measured thermometric coefficients α_v and his λ values show a trend with ice-point pressure p_0. No such trend[9] is evident when the corrections to zero pressure are made with the second virial coefficients, B_0 and B_{100}, for nitrogen determined by Henning and Heuse, Keesom and Tuyn, or Keyes.[10]

The best way to utilize Joule-Thomson coefficients for the correction of α_v, t_v, α_p, and t_p is probably the method proposed by Keyes,[10] in which he computes second virial coefficients, B, from the Joule-Thomson coefficients and heat capacities, and thus is able to average the results of the measurements of Joule-Thomson coefficients with those of compressibility measurements.

8. Summary of Observations, Data, and Formulae for Correction of the Measurements for a Constant Volume Gas Thermometer

(*a*) *Quantities Measured in Each Run*

H = vertical distance (mm.) from crown of mercury meniscus in short arm of main manometer to crown in long arm.

h_1 = height (mm.) of mercury meniscus in long arm of main manometer.

h_2 = height (mm.) of meniscus in short arm of main manometer.

h_3 = vertical distance (mm.) from crown of meniscus in short arm of main manometer to index mark in short arm.

t_s = mean temperature (° C. Int.) of the scale.

t_{Hg} = mean temperature (° C. Int.) of mercury in main manometer.

t_b = mean temperature (0° C. Int.) of main thermometer bulb.

t_r = nominal integral temperature (° C. Int.) of the run.

t_i = mean temperature (° C. Int.) of the i-th dead space of the main thermometer system (i = 1, 2, 3, . . . m).

H_a = vertical distance (mm.) from crown of mercury meniscus in short arm of auxiliary manometer to crown in long arm.

t_{Hga} = mean temperature (° C. Int.) of mercury in auxiliary manometer.

t_{da} = mean temperature (° C. Int.) of the dead space of the auxiliary thermometer.

H_e = vertical height (mm.) of mercury column in external manometer.

H_B = vertical height (mm.) of mercury column in barometer.

t_e = mean temperature of mercury in external manometer and barometer (mean room temperature).

(*b*) *Calibration Quantities*

ε = scale error (mm.); a function of H for a fixed value of D_2.

D_2 = scale division nearest index mark in short arm of main manometer.

d_1 = diameter (mm.) of long arm of main manometer; a function of H for a fixed value of D_2.

d_2 = diameter (mm.) of short arm of main manometer at index mark; a constant.

a_m = area (ml./mm.) of short arm of main manometer at index mark.

V_{bn} = volume (ml.) of main thermometer bulb under standard conditions.

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[7] See, for instance, F. G. Keyes and F. W. Sears, Proc. Nat. Acad. Sci., **11,** 38–41 (1925); J. R. Roebuck, Proc. Am. Acad. Arts Sci., **64,** 287–334 (1930), see p. 312; E. W. Washburn, Bur. of Stan. J. Res. **9,** 521–528 (1932).

[8] J. R. Roebuck and T. A. Murrell, *Temperature*, pp. 60–73, Reinhold Publishing Corp., New York, 1941.

[9] J. A. Beattie, *Temperature*, pp. 74–88, Reinhold Publishing Corp., New York, 1941.

[10] W. Heuse and J. Otto, Ann. der Physik (5) **2,** 1012–1030 (1929); W. H. Keesom and W. Tuyn, Kamerlingh Onnes Lab., Univ. of Leiden, Supplement No. **78,** 85 pp. (1936); F. G. Keyes, *Temperature*, pp. 45–59, Reinhold Publishing Corp., New York, 1941.

V_{in} = volume (ml.) of i-th main thermometer dead space under standard conditions ($i = 1, 2, 3, \ldots m$). V_{mn} is the volume in the short arm above a horizontal plane through the index mark plus Δ.

l_{bn} = vertical distance (mm.) from center of main thermometer bulb to the beginning of the first dead space under standard conditions.

l_{in} = vertical height (mm.) of the i-th dead space of the main thermometer system under standard conditions ($i = 1, 2, 3, \ldots m$). The algebraic sign of l is plus if the end nearer the bulb is below the farther end, otherwise minus.

δ_a = mean capillary depression correction for the auxiliary manometer.

r_{an} = ratio of volume of the dead space to the total volume of the auxiliary thermometer under standard conditions.

$\Phi_{an} = p'_{an}\left[\frac{1 - r_{an}}{T_{ban}} + \frac{r_{an}}{T_{dan}}\right]$ = calibration function for auxiliary thermometer. In this expression T_{ban} is the Kelvin temperature of the bulb of the auxiliary thermometer, T_{dan} the mean Kelvin temperature of the dead space, and p'_{an} the pressure in the calibration run.

g_l = acceleration of gravity (cm./sec.^{2}) at the laboratory.

R_0, α, δ, = ice point resistance and parameters in the Callendar equation for the platinum resistance thermometers.

(*c*) *Properties of Materials*

α_s = mean coefficient of linear thermal expansion (° C.$^{-1}$ Int.) of the material of the scale from t_{sn} to t_s.

ρ_s = density (gm./mm.^{3}) of the material of the scale.

E_s = Young's modulus (dynes/mm.^{2}) of the material of the scale.

δ = capillary depression (mm.) of the mercury in the main manometer.

α_{Hg} = mean coefficient of thermal dilation (° C.$^{-1}$ Int.) of mercury from 0° to $t°_{Hg}$ C.

β_{Hg} = mean coefficient of cubical compressibility (atm.$^{-1}$) of mercury from 0 to 3 atm. at mean room temperature.

$F = \frac{g_l}{g_n}\frac{1}{1 + \alpha_{Hg} t_{Hg}}$.

g_n = standard gravity, 980.665 cm./sec.^{2}

V_c = covolume (ml.) of mercury meniscus.

α_b = mean coefficient of thermal dilation (° C.$^{-1}$ Int.) of the material of the bulb of the main thermometer from $t°_{bn}$ to t_r° C.

α'_b = true coefficient of thermal dilation (° C.$^{-1}$ Int.) of the material of the bulb at t_r° C.

$\frac{\beta_b}{760}$ = mean coefficient of cubical compressibility (mm.$^{-1}$) of the material of the bulb from 0 to 3 atm. at t_r° C.

γ_b = mean dilation (ml./mm.) of the bulb due to difference between internal and external pressure at t_r° C.

α_i = mean coefficient of thermal dilation (° C.$^{-1}$ Int.) of the material of the i-th dead space of the main thermometer system from t_{in} to t_i° C. ($i = 1, 2, 3, \ldots m$).

α_v = mean coefficient of thermal pressure increase (° C.$^{-1}$ Int.) at constant volume from 0° to 100° C. of the thermometric gas. This value need be known only approximately.

M = molecular weight of the gas.

B = second virial coefficient (ml./mole) of the gas.

Subscript n denotes standard conditions.

(*d*) *Equations*

For the auxiliary thermometer. $p_a' = (H_a + \delta_a) F_a$

$$\frac{1}{T_1} = \frac{\frac{\Phi_{an}}{p'_a} - \frac{r_{an}}{T_{da}}}{1 - r_{an}}$$

For the external pressure control circuit. $p_e = (H_e + H_B)\, F_e$

$$p' - p_e = HF - (H_e + H_B)\, F_e$$

For the main thermometer. $p' = (H + \delta_1 - \delta_2 + \delta_3)\, F$

$$\delta_3 = \varepsilon_1 - \varepsilon_2 + \alpha_s H\,(t_s - t_{sn}) + \frac{\rho_s\, g_l}{2E_s} H\,(H + 2D_2) + \beta_{Hg}\, H\, \frac{HF - 760}{1520}$$

$$p = p' + \delta_4 + \delta_5 + \delta_6 + \delta_7 + \delta_8$$

$$\delta_4 = 1.1795 \times 10^{-6} M \frac{p' V_b}{V} \left(\frac{l_b}{T_b} + \sum_1^{m}{}_i \frac{l_i}{T_i} \right)$$

$$\delta_5 = \frac{p'}{V} \left[(V_b - V_{bn}) + \sum_2^{m}{}_i\, (V_i - V_{in}) \right]$$

$$\delta_6 = \frac{p'}{V} \left[V_{1n} \left(\frac{T_b}{T_1} - 1 \right) + \sum_2^{m}{}_i\, V_1 \left(\frac{T_b}{T_i} - 1 \right) \right]$$

$$\delta_7 = \frac{p'^2}{RV} \left[B_r \left(\frac{V_b - V}{T_r} + 2 \sum_1^{m}{}_i \frac{V_i}{T_i} \right) - T_r \sum_1^{m}{}_i \frac{B_i\, V_i}{T_i^2} \right]$$

$$\delta_8 = p_0\, \alpha_v\, (t_r - t_b)$$

$$V = V_{bn} + \sum_1^{m}{}_i\, V_{in}$$

$$V_b - V_{bn} = V_{bn} \left[\alpha_b\, (t_r - t_{bn}) + \alpha_b'\, (t_b - t_r) - \frac{\beta_b}{760}\, (p' - 760) \right] + \gamma_b\, (p' - p_e)$$

$V_i - V_{in} = V_{in}\, \alpha_i\, (t_i - t_{in})$ $\qquad (i = 2, 3, 4, \ldots m - 1)$

$V_m - V_{mn} = V_{mn}\, \alpha_m\, (t_m - t_{mn}) + \Delta V_m$

$\Delta V_m = a_m\, h_3 + V_c - \Delta.$

Δ = a number slightly less than the smallest value of $a_m\, h_3 + V_c$.

$T = t + T_0 + (T_{\text{abs.}} - T_{\text{Int.}})$; $t \equiv t^\circ$ C. (Int.)

l_b and l_i $(i = 1, 2, 3, \ldots m)$ depend on l_{bn} and l_{in}, $(t_b - t_{bn})$ and $(t_i - t_{in})$, $\alpha_b/3$ and $\alpha_i/3$, and the method of suspension of the bulb of the main thermometer; l_m also depends on h_3.

(*e*) *Tabulated Values*

F as a function of t_{Hg}.

δ_1 as a function of H and h_1.

δ_2 as a function of h_2.

δ_3 as a function of H and t_s

$\delta\left(\frac{t}{100}\right)\left(\frac{t}{100} - 1\right)$ as a function of t_{Pt} for the five platinum resistance thermometers used to determine t_{Hg} and t_m.

Critical tables giving V_i and $V_i - V_{in}$ as functions of t_i $(i = 2, 3, 4, \ldots m)$.

$V_c - \Delta$ as a function of h_2.

$V_{bn}\, \alpha_b\, t_r$ as a function of t_r.

$V_{bn}\, \alpha_b'$ as a function of t_r.

$V_{bn}\, \beta_b/760$ as a function of t_r.

γ_b as a function of t_r.

l_b/T_b as a function of t_r.

l_1/T_1 as a function of $1/T_1$.

l_i/T_i as a function of t_i and t_r $(i = 2, 3, 4, \ldots m - 1)$.

l_m/T_m as a function of t_m and h_2.

T° Kelvin as a function of t° C. Int.

B as a function of t.

9. Summary

The idealized constant volume and constant pressure gas thermometers are defined and the relations for the thermometric coefficients and gas temperatures given in terms of these definitions.

The deviations of the practical from the idealized gas thermometers are discussed and relations given for correction of the observations on the practical instrument for the deviations from ideality.

The complete theory of the use of the auxiliary gas thermometer for determination of the dead space correction in the region of large thermal gradient is given, and a test of the performance of the auxiliary thermometer is discussed.

Relations for the correction of the observed thermometric coefficients and gas temperatures for the imperfection of the thermometric gas are given.

(Contribution from the Research Laboratory of Physical Chemistry,
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AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE

VIII. THE THERMAL EXPANSION AND COMPRESSIBILITY OF VITREOUS SILICA AND THE THERMAL DILATION OF MERCURY

By James A. Beattie, B. Edwin Blaisdell, Joseph Kaye, Harold T. Gerry, and Clarence A. Johnson

TABLE OF CONTENTS

1. Introduction 371
2. Description of the Apparatus 371
3. Procedure 372
4. Derivation of the Equations 373
5. Results
(a) Linear Thermal Expansion of Vitreous Silica 375
(b) Compressibility of Vitreous Silica 378
(c) Thermal Dilation of Mercury 380
6. Summary 383

1. Introduction

In the reduction of the data resulting from gas thermometric measurements an accurate knowledge of the dilation of the bulb caused by variations in temperature and in internal and external pressure is required. We used bulbs of vitreous silica[1] because of the low thermal dilation of this material.

In order to record the thermal dilation of the bulbs in terms of that of mercury, we determined the apparent thermal dilation of mercury in the two vitreous silica bulbs used by us over the temperature range 0° to 350° C. At the same time the dilation of the bulbs caused by a difference between inside and outside pressure was measured at several temperatures. Later a cylindrical ring of vitreous silica was prepared from one of the bulbs and its linear thermal expansion in the temperature range − 200° to + 450° C. determined by an interference method.

From these results and data on the rigidity of vitreous silica, it was possible to compute the mean coefficient of linear thermal expansion and mean coefficient of compressibility of vitreous silica, and the mean coefficient of thermal dilation of mercury. These results are compared with those of other investigators in Tables III, VI, and IX. Equations expressing these quantities as functions of temperature are given in the Summary, and these and derived quantities are tabulated for various temperatures in Tables X to XVIII.

2. Description of the Apparatus

(a) *Apparent Thermal Dilation of Mercury*

A sketch of one of the bulbs is shown in Fig. 1. The bulbs, designated as "Red" and "Green," were the two used in the final gas thermometric measurements[1] (Runs 111 to 394) and each had a volume of about 1000 ml. The pyrex capillary and graded seal attached to the bulb in the earlier measurements were replaced by a vitreous silica capillary of about 0.9 mm. bore. The welded steel case surrounding the bulb was fitted with a three-piece steel liner accurately shaped to fit the external surface of the bulb with a clearance of 0.5 mm. and a push fit in the case. The connection between the silica capillary and metal tube at the top was made by means of a heavy rubber tube. The left-hand side arm near the top of the metal tube was for the introduction of mercury into the case and the application of gas pressure or suction; and the right-hand tube was for the overflow of mercury from the case. The numbers are distances in centimeters measured from the top of the thermostat cover.

The tip of the silica capillary was placed beneath the surface of mercury in a weighing bottle

[1] J. A. Beattie, D. D. Jacobus, J. M. Gaines, Jr., M. Benedict, and B. E. Blaisdell, Proc. Am. Acad. Arts Sci., **74**, 327-342 (1941).

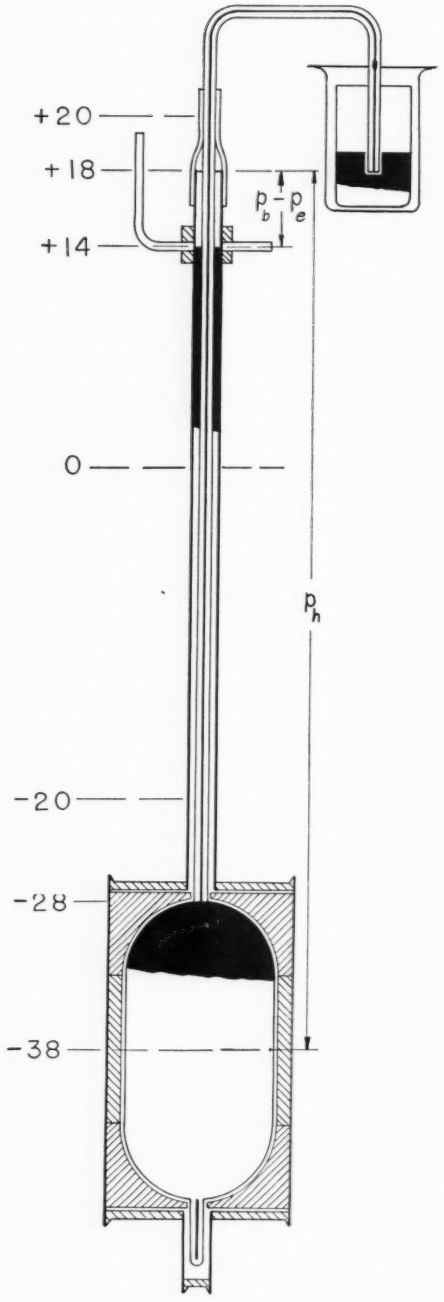

FIG. 1. Sketch of the apparatus. The numbers are the distances in centimeters measured from the top of the thermostat cover.

held in a beaker which had a fairly tight-fitting cover that effectively prevented circulation of air but not equilibration of pressure between outside and inside.

The bulb floated in a bath of mercury contained in the metal case and always made contact with the upper hemispherical surface of the liner.

(b) *Linear Thermal Expansion of Vitreous Silica*

A cylindrical ring of vitreous silica 3 cm. in diameter, 2 cm. long and 2 mm. thick (the thickness of the bulb) was made from the Green bulb and annealed in the same manner as the bulbs. The change in length of the sample with change in temperature was measured by the absolute Fizeau method with a Pulfrich interferometer manufactured by Zeiss. In this method the sample itself is used to separate the top and bottom reflecting plates. Because of the large separation of the plates the intensity of the bands is low. The intensity was increased to a satisfactory visibility by sputtering the reflecting surfaces with platinum. In order to decrease the chance of relative motion of the sample and plates, the top plate was held down by a 50 gram weight. The source of light was the mercury green line for which $\lambda = 54.6224 \times 10^{-6}$ cm. in vacuo and in the helium of the density used in our experiments.

The thermostats were gas-tight and contained helium at a pressure of 2 mm. of mercury at room temperature. In one thermostat the expansion in the range $-200°$ to $+100°$ C. was studied; in a second that in the range 25° to 450° C. investigated.

The true length of the cylinder at 0° C. was $l_0 = 1.9368$ cm.

3. PROCEDURE

(a) *Apparent Thermal Dilation of Mercury*

The bulbs and cases were evacuated for several days while at a temperature of 400° C., and both were then filled in vacuo with mercury that had been distilled twice in air at 20 mm. pressure and once in vacuo. The mercury entered the systems through barometric columns and fell through two meters of tubing bent in a spiral.

The two bulbs and four standard platinum resistance thermometers were placed in the oil bath used in the gas thermometric measurements. The upper ends of the silica capillaries were placed beneath the surface of mercury in the weighing bottles and the system maintained

overnight at a temperature close to the desired value. In the morning the system was brought to the desired temperature and automatic regulation maintained for one hour. The weighing bottle was replaced by a second bottle and the mass of mercury in the first computed from weighings made in air against brass standards. After one half an hour the second bottle was weighed to determine the gain or loss of mercury. The variation in the mass of mercury in the second bottle was less than 5×10^{-4} gm. in all runs.

The thermostat temperature was then changed to a new value and the process repeated.

In the oil bath runs were made from 0° to 150° C. The bulbs and resistance thermometers were then transferred to the nitrate bath and runs from 150° to 350° C. made. In each series most of the temperatures were approached from above and from below. In the low temperature series the temperature 152.315° was used unintentionally instead of 150° C. In the nitrate bath runs were made at both temperatures.

When the weighing bottle was removed the mercury ran back into the silica capillary for a short distance. The position of the meniscus was reproducible to $\pm$ 1 mm. in most cases and no correction was made for this effect when the position was thus reproduced. For several of the runs in succession the position of the meniscus differed appreciably from the normal position and a tip correction was applied. The normal position was resumed after the tip of the capillary had been cleansed by being raised to white heat.

At each temperature (but not for each run) the temperature distribution along the capillary in the region of large thermal gradient was determined by a thermocouple.

At 25°, 100°, 200°, and 300° C. the dilation of the bulb caused by a variation of external pressure, internal pressure being constant, was determined. The tip of the silica capillary was placed beneath the surface of mercury and suction applied to the case until the pressure at the side arm as indicated on an open manometer was about 700 mm. below atmospheric. The weighing bottle was replaced by an empty one and the pressure adjusted until the drop of mercury protruding from the capillary was 0.40 mm. high. The pressure in the side arm was then raised to about atmospheric and again adjusted until the drop had the same height. The mass of mercury forced out of the bulb was determined. Four determinations were made at each temperature.

(b) *Linear Thermal Expansion of Vitreous Silica*

The cylindrical ring of vitreous silica was placed in the thermostat with the reflecting plates top and bottom and a metal cylindrical ring weighing 50 gms. placed on the top plate. The necessary adjustments for proper reflection into the interferometer were made. The thermostat chamber was closed gas-tight and filled with helium to a pressure of 2 mm. at room temperature.

The thermostat was regulated automatically[1] at some temperature; and after one hour of satisfactory regulation ($\pm$ 0.005° C.) the temperature and the micrometer reading for the index circle and the two bands on each side were determined. The process was repeated at other temperatures, the number of bands passing by the index circle during change in temperature being counted.

Temperatures were determined by platinum resistance thermometers: those below 0° C. were transferred to the absolute scale by comparison of the readings of the resistance thermometer with the indications of a constant volume hydrogen gas thermometer; and those above 0° C. were on the International Scale.

The band reading of the index was computed to 0.01 band by the method of least squares. Plots of band readings against temperature showed discontinuities at several places indicating that slipping of the plates or sample had occurred. Thus although all of the low temperature and all of the high temperature runs were each made in one continuous series, it was necessary to treat each set as several series.

4. Derivation of the Equations

Let: p = pressure (in atm. unless otherwise stated).

V = volume (ml.).

t = Centigrade temperature (° C. Int. unless otherwise stated).

M = grams of mercury.

δ = density (gm./ml.).

Subscript Hg denotes that the quantity applies to mercury.

Subscript b denotes the bulb.

Subscript i (i = 1, 2, 3, . . . m) denotes the i-th section of the capillary.

Subscript w denotes the weighing bottle.

Subscript 0 denotes the value of a quantity at the standard conditions of calibration 0° C. and 1 atm. pressure.

Subscript r denotes the nominal (integral) International temperature of the thermostat for a run. Thus if $t_b = 150.0018°$, $t_r = 150°$ C.

p_e = external pressure on the bulb in a plane passing horizontally through the center.

p_h = pressure caused by head of mercury (see Fig. 1).

p_B = corrected barometric pressure.

α = mean coefficient of thermal dilation, $(1/V_0)\,(\Delta V/t)°\,\text{C.}^{-1}$, from 0° to t_i° C. for the capillary sections and the contained mercury, and from 0° to t_r° C. for the bulb and contained mercury, pressure being 1 atm.

α' = true coefficient of thermal dilation, $(1/V_0)\,(dV/dt)°\,\text{C.}^{-1}$, at t_r° C. and 1 atm. pressure.

β = mean coefficient of compressibility, $-(1/V_{t_r})\,(\Delta V/\Delta p)$ atm.$^{-1}$, at low pressure and at t_r° C. where V_{t_r} is the volume at t_r° C. and 1 atm.

γ = mean dilation, $\Delta V_b/(p_b - p_e)$ ml. atm.$^{-1}$, of the bulb at t_r caused by the difference between internal pressure p_b and external pressure p_e.

$C_b = \delta_{Hg0}\,\gamma_b/(1 + \alpha_{Hg}\,t_r)$ gm. Hg atm.$^{-1}$ = grams of mercury forced out of the bulb per atmosphere increase in $p_b - p_e$ at t_r. We measured C_b and computed γ_b from the above equation.

The volume V_b of the bulb at $(t_b,\ p_b,\ p_e)$ is given by the expression:

$$V_b = V_{b0}\,[1 + \alpha_b t_r + \alpha_b'\,(t_b - t_r)] \times [1 - \beta_b\,(p_b - 1)] + \gamma_b\,(p_b - p_e); \quad (1)$$

and the density of the mercury in the bulb by the equation:

$$\delta_{Hg} = \delta_{Hg0}\,[1 + \alpha_{Hg}\,t_r + \alpha'_{Hg}\,(t_b - t_r)]^{-1} \times [1 - \beta_{Hg}\,(p_b - 1)]^{-1} \quad (2)$$

The volume of the i-th section of capillary at t, assumed independent of pressure, is

$$V_i = V_{i0}\,(1 + \alpha_i\,t_i); \quad (i = 1, 2, 3, \ldots m) \quad (3)$$

and the density of mercury in the i-th capillary is taken to be

$$\delta_{Hg} = \delta_{Hg0}\,(1 + \alpha_{Hg}\,t_i), \quad (4)$$

independent of pressure.

The total mass of mercury in the system (bulb, capillary, weighing bottle) is constant for a complete series of runs. At any bulb temperature, t_b, this mass is:

$$M = M_{b0}\,\frac{[1+\alpha_b t_r+\alpha_b'(t_b-t_r)]\,[1-\beta_b(p_b-1)]}{[1+\alpha_{Hg}t_r+\alpha'_{Hg}(t_b-t_r)]\,[1-\beta_{Hg}(p_b-1)]} + C_b(p_b-p_e) + \sum_1^m{}_i\, M_{i0}\,\frac{1+\alpha_i t_i}{1+\alpha_{Hg}t_i} + M_{wt_b} \quad (5)$$

$$= M_{b0}\,\frac{1+\alpha_b t_r}{1+\alpha_{Hg}t_r} + \sum_1^m{}_i\, M_{i0} + M_{wt_r}; \quad (6)$$

where

$$M_{wt_r} = M_{wt_b} + \Delta M_{bt_b} + \sum_1^m{}_i\, \Delta M_{it_i}, \quad (7)$$

$$\Delta M_{bt_b} = M_{b0}\left\{\frac{\alpha'_b\,(1+\alpha_{Hg}t_r) - \alpha'_{Hg}(1+\alpha_b t_r)}{(1+\alpha_{Hg}t_r)^2}\times (t_b-t_r) + \frac{1+\alpha_b t_r}{1+\alpha_{Hg}t_r}\,(\beta_{Hg}-\beta_b)\,(p_b-1)\right\} + C_b\,(p_b-p_e), \quad (8)$$

$$\Delta M_{it_i} = M_{i0}\,\frac{t_i\,(\alpha_i-\alpha_{Hg})}{1+\alpha_{Hg}t_i}. \quad (i = 1, 2, 3, \ldots m) \quad (9)$$

In the above expressions M_{b0} and M_{i0} are the number of grams of mercury of standard density —13.59546 gms./ml.—in the bulb and the i-th capillary section, respectively, when each is at 0° C. and under 1 atm. internal and external pressure; M_{wt_b} is the actual number of grams of mercury in the weighing bottle when the bulb is at t_b and the capillary sections at t_i; and M_{wt_r} is the corrected number of grams of mercury which would have been in the weighing bottle if: (1) the bulb temperature had been t_r, (2) the external and internal pressures had been constant throughout the system and had had the value 1 atm., and (3) the capillary sections 1 to m had been at 0° C. and 1 atm. pressure (thus containing the same mass of mercury at all bulb temperatures).

The approximations made in deriving the above equations introduce an error of less than 1×10^{-5} grams of mercury.

Applying equation (6) to $t_r = 0$ and $t_r = t$ and equating the two values of M, we obtain:

$$\alpha_{Hg} = \frac{m}{t\,(M_{b0}-m)} + \frac{M_{b0}\,\alpha_b}{M_{b0}-m}, \quad (10)$$

where

$$m = M_{wt} - M_{w0} \quad (11)$$

is the corrected number of grams of mercury that flows into the weighing bottle when the bulb is heated from 0° to t° C. The quantity

$$\alpha_{Hg}\,(\text{apparent}) = \frac{m}{t\,(M_{b0}-m)} \quad (12)$$

is called the apparent mean coefficient of thermal dilation of mercury in the material composing the bulb.

5. Results

(a) *Linear Thermal Expansion of Vitreous Silica*

The band reading was multiplied by $10^6\lambda/2l_0$ ($= 10^6 \times 54.6224 \times 10^{-6}/2 \times 1.9368 = 14.1012$) to give $[10^6\ (l-a)/l_0]_{obsd.}$, the length of the sample (in units of $10^6/l_0$) at the temperature t, except for the parameter a that is constant for any one series of runs, but varies from series to series on account of the slippage. All of the values of $[10^6\ (l-a)/l_0]_{obsd.}$ were plotted against t on a single plot, the pieces of the curves corresponding to different series being moved as a whole parallel to the length axis until a single curve could be drawn through all of the series of points. From points read from this curve an equation similar to Eq. (A), Table I, was derived expressing $[10^6\ (l-l_0)/l_0]_{obsd.}$ as a function of t. The values $[10^6\ (l-l_0)/l_0]_{calcd.}$ were computed from this equation for each temperature at which a measurement was made. We determined a for each series as

$$10^6\,(a-l_0)/l_0 = \frac{\Sigma\,[10^6\,(l-l_0)/l_0]_{calcd.} - \Sigma\,[10^6\,(l-a)/l_0]_{obsd.}}{\text{number of measurements in series}}.$$

Hence:

$$[10^6\,(l-l_0)/l_0]_{obsd.} = [10^6\,(l-a)/l_0]_{obsd.} + 10^6\,(a-l_0)/l_0.$$

Thus a was determined from all of the measurements in any one series and not alone from the observations near 0° C.

The values of $[10^6\,(l-l_0)/l_0]_{obsd.}$ so derived were again expressed as a function of t; and new, slightly different, values of a obtained. The process was repeated a third time, no significant difference in the values of a being found.

The results are given in Table I. In the first column are listed the temperatures on the thermodynamic scale when below 0° C. and on the International scale when above 0°; in the second are given the observed values of $10^6\ (l-l_0)/l_0$ obtained as described above; and in the third the value computed from Eq. (A).

TABLE I

Linear Thermal Expansion of Vitreous Silica

$$10^6 \times (l-l_0)/l_0\ (\text{calcd.}) = \frac{t^2 + 157.361t}{0.00126792t^2 + 0.88121t + 412.109} \qquad (-175° < t°\ \text{C.} < +450°) \quad (A)$$

$$10^6 \times (V-V_0)/V_0 = \frac{t^2 + 157.281t}{0.0004225t^2 + 0.29362t + 137.32} \qquad (-175° < t°\ \text{C.} < +450°) \quad (B)$$

Temp.[1]	$10^6 \times (l-l_0)/l_0$			Temp.[1]	$10^6 \times (l-l_0)/l_0$			Temp.[1]	$10^6 \times (l-l_0)/l_0$		
°C.	Obsd.	Calcd.	Obsd.-calcd.	°C.	Obsd.	Calcd.	Obsd.-calcd.	°C.	Obsd.	Calcd.	Obsd.-calcd.
Low Temperature Measurements											
Series A1				− 76.37	−16.894	−17.562	+0.668	−157.09	− 0.591	− 0.140	−0.451
+ 26.14	+11.666	+11.001	+0.665	− 55.99	−15.624	−15.476	−0.148	−189.28[2]	+20.419	+20.780	−0.361
− 8.65	− 3.564	− 3.179	−0.385	− 28.82	− 9.844	− 9.554	−0.290	−218.49[2]	+43.259	+47.683	−4.424
− 40.60	−12.584	−12.527	−0.057	− 4.02	− 1.804	− 1.509	−0.295	−190.02[2]	+20.559	+21.367	−0.808
− 88.05	−17.804	−17.723	−0.081	+ 23.63	+10.466	+ 9.863	+0.603	−168.33	+ 6.039	+ 6.161	−0.122
−117.63	−13.574	−14.336	+0.762	+ 53.27	+24.986	+24.252	+0.734	−132.12	− 9.761	−10.493	+0.732
−142.93	− 7.514	− 6.610	−0.904	+ 82.35	+39.936	+40.019	−0.083	−102.41	−15.821	−16.790	+0.969
−186.42[2]	+16.886	+18.559	−1.673	Series A3				− 64.22	−16.241	−16.581	+0.340
−216.01[2]	+41.566	+45.097	−3.531	+107.45	+55.109	+54.569	+0.540	− 79.56	−19.211	−17.684	−1.527
Series A2				+ 82.95	+40.299	+40.358	−0.059	− 65.39	−17.371	−16.710	−0.661
−195.61[2]	+22.456	+25.956	−3.500	+ 53.55	+22.959	+24.397	−1.438	− 10.42	− 4.541	− 3.799	−0.742
−177.81[2]	+10.186	+12.304	−2.118	− 11.30	− 3.131	− 4.102	+0.971	+ 45.85	+20.979	+20.469	+0.510
−155.88	− 1.094	− 0.756	−0.338	− 80.57	−18.921	−17.711	−1.210	+ 99.28	+50.169	+49.755	+0.414
−125.67	−14.214	−12.392	−1.822	−105.55	−15.821	−16.411	+0.590	+ 12.70	+ 4.909	+ 5.100	−0.191
− 97.03	−16.324	−17.292	+0.968	−127.22	−11.031	−11.963	+0.932	+ 13.95	+ 6.039	+ 5.628	+0.411

[1] Degrees C. absolute below 0°; degrees C. International above 0°.

[2] Points not used in fitting the equation; deviations not included in averages.

TABLE I—*Continued*

High Temperature Measurements

Series B1				Series B4				50	23.499	22.572	+0.927
25	10.577	10.482	+0.095	150	80.398	80.486	−0.088	350	203.459	202.747	+0.712
50	23.197	22.572	+0.625	100	49.198	50.177	−0.979	150	78.839	80.486	−1.647
75	35.997	35.908	+0.089	250	142.788	143.103	−0.315	150	79.829	80.486	−0.657
100	49.367	50.177	−0.810	300	174.598	173.553	+1.045	200	111.219	111.838	−0.619
Series B2				200	112.648	111.838	+0.810	350	203.609	202.747	+0.862
75	36.337	35.908	+0.429	250	142.628	143.103	−0.475	400	231.479	230.443	+1.036
100	50.547	50.177	+0.370	Series B5				450	257.459	256.533	+0.926
50	22.927	22.572	+0.355	50	23.014	22.572	+0.442	Series B7			
25	9.327	10.482	−1.155	350	202.304	202.747	−0.443	100	50.486	50.177	+0.309
Series B3				Series B6				350	201.876	202.747	−0.871
50	21.440	22.572	−1.132	200	111.759	111.838	−0.079	300	173.036	173.553	−0.517
150	80.360	80.486	−0.126	400	229.009	230.443	−1.434	400	230.696	230.443	+0.253
250	143.960	143.103	+0.857	300	173.169	173.553	−0.384	250	142.806	143.103	−0.297
350	203.740	202.747	+0.993	150	80.339	80.486	−0.147	50	24.066	22.572	+1.494
450	255.940	256.533	−0.593	400	231.119	230.443	+0.676	100	50.566	50.177	+0.389
				100	51.009	50.177	+0.832	300	173.756	173.553	+0.203
				200	110.839	111.838	−0.999	450	255.566	256.533	−0.976

Series	Number of points	Average deviation	Root-mean-square deviation
A	35	0.618×10^{-6}	0.7496×10^{-6}
B	45	0.655×10^{-6}	0.7634×10^{-6}
A+B	80	0.638×10^{-6}	0.7574×10^{-6}

TABLE II

DEVIATIONS OF THE OBSERVED FROM THE CALCULATED VALUES OF THE LINEAR THERMAL EXPANSION OF VITREOUS SILICA FROM 0° TO t° C.

THE RESULTS ARE DERIVED FROM TABLE I

Temp. °C.	Number of Points	Obsd. minus calcd. Values of $\frac{l - l_0}{l_0} \times 10^6$			
		Sum of Positive	Sum of Negative	Algebraic Sum	Algebraic Average
Low Temperature Measurements					
−175 to −125	7	1.664	3.637	−1.973	−0.282
−125 to − 75	8	3.957	2.818	+1.139	+0.142
− 75 to − 25	5	0.340	1.156	−0.816	−0.163
− 25 to + 25	6	1.382	1.613	−0.231	−0.038
+ 25 to + 75	5	2.512	1.438	+1.074	+0.215
over + 75	4	0.954	0.142	+0.812	+0.203
High Temperature Measurements					
25	2	0.095	1.155	−1.060	−0.530
50	6	3.843	1.132	+2.711	+0.452
75	2	0.518	0.000	+0.518	+0.259
100	6	1.900	1.789	+0.111	+0.018
150	5	0.000	2.665	−2.665	−0.533
200	4	0.810	1.697	−0.887	−0.222
250	4	0.857	1.087	−0.230	−0.058
300	4	1.248	0.901	+0.347	+0.087
350	5	2.567	1.314	+1.253	+0.251
400	4	1.965	1.434	+0.531	+0.133
450	3	0.926	1.560	−0.634	−0.211
Arithmetic average					0.223

TABLE III

COMPARISON OF OUR VALUES OF THE MEAN COEFFICIENT OF LINEAR THERMAL EXPANSION FROM 0° TO t° C. OF VITREOUS SILICA WITH THE MEASUREMENTS AND THE SELECTED VALUES OF OTHER AUTHORS

$10^8\,\alpha$ (linear) $= a + bt + ct^2$

Author	a	$b \times 10^2$	$c \times 10^4$	Range of validity (° C.)
Chappuis (1903)	38.474	11.5		0 to 83
Donaldson (1912)	38	11		0 to 30
Callendar (1913 A)	29	25	−7	− 20 to +150
Scheel (1914)	36.2	18.13	−3.40	−253 to +100
Scheel (1921)	39.5	12.82	−1.698	100 to 500
Souder, Hidnert (1926)	33.9	21.61		−183 to 0

Callendar (1913 B) $10^8\,\alpha$ (linear) $= 78.0 - \dfrac{8650}{t + 175}$ 0 to 300° C.

Harlow (1929) $10^8\,\alpha$ (linear) $= 66.3 - \dfrac{3879}{t + 103}$ 0 to 300° C

Temp. ° C.	$10^8\,\alpha$ (linear) °C.$^{-1}$										
	Chappuis	Henning[1]	Randall[1]	Donaldson	Callendar[2]	Scheel[3]	Souder Hidnert[1]	Wheeler Summary	Sosman Summary	Harlow Summary	Our Values
	1903	1907	1910	1912	1913	1914 1921	1926	1914	1927	1929	1940
−150						1.4	1.5	0.0	− 3.3		2.4
−125						8.2	6.9	7.0			10.1
−100						14.7	12.3	14.3	+13.3		17.0
− 75						20.7	17.7	21.2			23.3
− 50						26.3	23.1	27.0	25.0		28.9
− 25					22.3	31.5	28.5	31.2			33.9
0	38.5			38.0	29.0	36.2	33.9		38.3	28.6	38.2
+ 25	41.3			40.8	34.8	40.5		39.4		36.0	41.9
50	44.2				39.8	44.4		42.8	43.3	40.9	45.1
75	47.1		41.0		43.8	47.9		46.1		44.5	47.9
100			43.5		47.0	50.9	43.6	48.8	48.3	47.2	50.2
150			47.6		51.4	54.9		51.5	51.7	51.0	53.7
200			50.5		54.9	58.3	48.8	52.5	53.3	53.5	55.9
250		52.8	52.5		57.6	60.9		54.0		55.3	57.2
300			53.9		59.8	62.7	52.0	55.3	55.7	56.7	57.9
350			54.9			63.6		55.7			57.9
400			55.6			63.6	54.2	55.5	56.7		57.6
450			56.0			62.8		55.8			57.0
500		53.4	56.2			61.2	51.4	55.8	56.7		

[1] Corrected from 16-to-t or 20-to-t to 0-to-t by use of α (linear) $\times 10^8 = 38.0$ from 0-to-16 or 0-to-20.

[2] Values −25 to +100 from (1913A) equation; 150 to 300 from (1913B) equation.

[3] Values −150 to +100 from (1914) equation; 150 to 500 from (1921) equation. The values in this column agree with the Wärmetabellen summary.

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Eq. (B) given in Table I was obtained from Eq. (A) by approximation. The values of $(V - V_0)/V_0$ computed from Eqs. (A) and (B) agree to 0.01×10^{-6} from 0° to 450° C., the difference increasing below 0° to 0.15×10^{-6} at − 175° C. The agreement is far better than the accuracy of the data.

In Table II the residuals of Table I are added algebraically in each 50° temperature range for the low temperature runs and at each temperature for the high temperature series. The results indicate that the equation follows the trends of the measurements quite well to − 175° C. which is below the temperature of minimum length, − 84.6° C. The root-mean-square deviations $(\Sigma v^2/n)^{1/2}$ of $(l - l_0)/l_0$ from the four-constant equation, Eq. (A), are given in Table I and the average of the algebraic average of the residuals in each temperature range in Table II. The probable error of a single determination computed from the residuals given in Table I is 0.562×10^{-6} in $(l - l_0)/l_0$ (80 points, 10 series, 4 constant equation); the reproducibility of a single reading was about one twentieth of a band width or 0.7×10^{-6} in $(l - l_0)/l_0$.

In Table III the results of the present investigation are compared with the values given by other workers, and the summaries of Wheeler, Sosman, and Harlow. The agreement with Sosman's selected values is fair.

(b) *Compressibility of Vitreous Silica*

In Table IV are given the results of the measurements of the number of grams of mercury forced out of the bulbs at several temperatures when the external pressure p_e was increased from about $p_b - 700$ mm. to about p_b. The internal pressure $p(= p_B + p_h)$ remaining constant at about 1.7 atm. to within ± 0.3 mm. Hg in any one experiment, but varying by as much as 1 mm. Hg (due to variation in p_B) from experiment to experiment at one temperature, and by as much as 25 mm. from 25° to 300° due to variation in p_h. No correction was made for these effects which affect the measurements by an amount less than the error of weighing. The number of grams of mercury that ran out, or the corresponding change in the volume of the bulb, divided by the final minus the initial value of p_e gives the effect produced by a unit change in $p_b - p_e$, p_b remaining constant.

Each of the values of C (gm. Hg/standard mm. Hg) in Table IV is the mean of four, the average deviation being about 1%. The quantities C were converted to the corresponding dilations of the bulb γ in ml./mm. Hg by division by the density of mercury at t. The least square equations for C and γ expressed as linear functions of temperature are given in the heading of Table IV and the deviations of the calculation from the observed values in the body of the table.

In Table V the dilations given in Table IV are used to compute the mean coefficient of compressibility of vitreous silica at low pressure. In the computation we assumed: (1) each bulb behaved as though it were a thin spherical shell plus a thin cylindrical shell with unconstrained ends; (2) the bulbs were of uniform thickness so that the dimensions of the parts could be computed from the mass, internal volume, and external diameter. The error introduced by the first assumption as regards the effect of the interaction of the hemispherical caps and the cylinder at the planes of jointure can be estimated[2] and is less than the errors of the data.

[2] E. Meissner, Schweizerische Bauzeitung, **86**, 1–5 (1925).

TABLE IV

DILATION OF THE VITREOUS SILICA BULBS CAUSED BY A DIFFERENCE BETWEEN INTERNAL AND EXTERNAL PRESSURE

C_b = grams of mercury forced out of the bulb per standard mm. Hg decrease in $p_b - p_e$.
$\gamma_b = C_b/\delta_{Hg}$ = ml. increase in volume of bulb per standard mm. Hg increase in $p_b - p_e$.

Equations: Red Bulb: $10^3 C_b = 0.9700 - 3.43 \times 10^{-4} t$ (A)
$10^3 \gamma_b = 0.0714 - 1.3 \times 10^{-5} t$ (B)
Green Bulb: $10^3 C_b = 1.1172 - 3.61 \times 10^{-4} t$ (C)
$10^3 \gamma_b = 0.0822 - 1.3 \times 10^{-5} t$ (D)

t ° C. (Int.)	δ_{Hg} gm./ml.	Red Bulb				Green Bulb			
		$C_b \times 10^3$		$\gamma_b \times 10^3$		$C_b \times 10^3$		$\gamma_b \times 10^3$	
		Obsd.	Obsd.-Eq. A	Obsd.	Obsd.-Eq. B	Obsd.	Obsd.-Eq. C	Obsd.	Obsd.-Eq. D
25	13.5340	0.9648	+0.0034	0.07129	+0.00021	1.1108	+0.0026	0.08207	+0.00019
100	13.3518	.9349	− .0008	.07002	− .00008	1.0801	− .0010	.08090	.00000
200	13.1127	.8935	− .0079	.06814	− .00066	1.0397	− .0053	.07929	− .00031
300	12.8747	.8723	+ .0052	.06775	+ .00025	1.0124	+ .0035	.07863	+ .00033

Note: Each tabulated value of C_b is the average of four measurements with an average deviation of 1%.

TABLE V

Calculation of the Mean Coefficient of Compressibility of Vitreous Silica

$\gamma_b = (A\beta + B/\mu)(p_i - p_e)$.

p_i was constant; p_e was varied; γ_b is given in Table IV.

$\beta = -(1/V_t)(\Delta V/\Delta p)_t$ or $-(1/V_0)(\Delta V/\Delta p)_t$; same value for vitreous silica to number of significant figures given (V_t is volume at $t°$ C. and 1 atm.; V_0 at 0° C. and 1 atm.).

μ = rigidity

$$A = \left(\frac{V_eV_i}{V_e - V_i}\right)_{\text{sphere}} + \left(\frac{V_eV_i}{V_e - V_i}\right)_{\text{cylinder}}; \quad B = \tfrac{3}{4}\left(\frac{V_eV_i}{V_e - V_i}\right)_{\text{sphere}} + \left(\frac{V_eV_i}{V_e - V_i}\right)_{\text{cylinder}}$$

e denotes external; i denotes internal; b denotes the bulb.

		Red Bulb		Green Bulb	
		δ_b = 2.208 gm. ml.$^{-1}$			
Mass (measured)		270.0 gm.		249.0 gm.	
V_e		1108.6 ml.		1128.2 ml.	
V_i (measured)[a]		986.3		1015.4	
r_e (measured)		4.225 cm.		4.245 cm.	
r_i		4.014		4.053	
length of cylinder		14.135		14.269	
thickness		0.211		0.192	
		Sphere	Cylinder	Sphere	Cylinder
V_e		315.9 ml.	792.7 ml.	320.4 ml.	807.8 ml.
V_i		270.9	715.5	278.9	736.4
A		9249 (1 + $\alpha_b t_b$) ml.		10485 (1 + $\alpha_b t_b$) ml.	
B		8773 (1 + $\alpha_b t_b$)		9946 (1 + $\alpha_b t_b$)	
Temp.	$\mu \times 10^{-5}$[b]	$\gamma_b \times 760$	$\beta \times 10^6$	$\gamma_b \times 760$	$\beta \times 10^6$
°C. (Int.)	atm.	ml./atm.	atm.$^{-1}$	ml./atm.	atm.$^{-1}$
25	2.964	0.05418	2.66	0.06237	2.75
100	2.985	.05322	2.58	.06148	2.69
200	3.013	.05179	2.45	.06026	2.60
300	3.040	.05149	2.44	.05976	2.58

[a] Without capillary ends.

[b] F. Horton, Phil. Trans. Royal Soc. London, **204A**, 407–431 (1905).

TABLE VI

Comparison of the Mean Coefficient of Compressibility of Vitreous Silica with the Values of Other Investigators

Equations: $\beta \times 10^6$ (atm.$^{-1}$) = $2.70 - 6 \times 10^{-4}t$ (A)

$\beta \times 10^9$ (mm. Hg^{-1}) = $3.55 - 8 \times 10^{-4}t$ (B)

	$\beta \times 10^6$ atm.$^{-1}$					
Temp. ° C.	Red	Green	Mean	Eq. A.	Birch, Dow[1]	Others[2]
0				2.70	2.57	
25	2.66	2.75	2.70	2.68		2.68–2.72
100	2.58	2.69	2.64	2.64	2.60	
200	2.45	2.60	2.52	2.58	2.51	
300	2.44	2.58	2.51	2.52	2.45	
400				2.46	2.48	

[1] F. Birch and R. B. Dow, Bull. Geol. Soc. Am., **47**, 1235–1255 (1936).

[2] R. B. Sosman, *International Critical Tables*, Vol. IV, p. 21 (1928), selects 2.72; L. H. Adams and R. E. Gibson, J. Wash. Acad. Sci., **21**, 381–390 (1931), obtain 2.72; F. Birch and R. R. Law, Bull. Geol. Soc. Am., **46**, 1219–1249 (1935), obtain 2.68, F. Birch, J. Applied Phys., **8**, 129–133 (1937), computes 2.69. All are for temperatures in the neighborhood of 25° C. and for low pressures.

The error introduced by the assumption of uniform thickness and precise shape is unknown. Measurement of the thickness of a broken bulb showed that there was a fair variation. The rigidity term (B/μ) $(p_i - p_e)$ accounts for about one half of ΔV_b so that our computation of β are quite dependent on the measurements of Horton, who used vitreous silica fibers.

In Table VI the values of the mean coefficient of compressibility of vitreous silica derived in Table V are given together with the results of other investigators and the equations we used to express β as a function of temperature. Our two bulbs gave values about 5% apart due no doubt to the assumption of uniform thickness. Our average values are in good agreement with the work of other investigators at 25°; and are within about 2% of the measurements of Birch and Dow at and above 100° C.

(c) *Thermal Dilation of Mercury*

The corrected mass M_{wt_τ} of mercury in the weighing bottles was computed by Eqs. (7) to (9) from the measured mass M_{wt_b} and the following data.

From the indications of the thermocouple for each thermostat temperature we determined from plots of temperature against distance: (1) the average temperature t_β from − 38 to + 18 (Fig. 1); (2) the average temperature t_γ from − 28 to + 14; and the three average temperatures t_i $(i = 1, 2, 3)$ into which the dead space from − 20 to + 20 was divided.

Then:

$$p_b(\text{atm.}) = p_B(\text{atm.}) + \frac{560\,[1 + \alpha_b(\text{linear})t_\beta]}{760\,(1 + \alpha_{Hg}\,t_\beta)}$$

$$p_b - p_e(\text{mm. Hg}) = 37 - \frac{420\,[\alpha_s(\text{linear}) - \alpha_b(\text{linear})]\,t_\gamma}{1 + 27\,\alpha_{Hg}}$$

where the subscript s denotes steel.

The true and the mean coefficients of thermal dilation and the mean coefficient of linear thermal expansion of vitreous silica are given in Tables XV to XVII. The mean coefficient of cubical compressibility of vitreous silica is given in Table VI, and the dilation of the bulbs caused by a difference between internal and external pressure in Table IV. The mean coefficient of linear thermal expansion of steel, and the true and the mean coefficients of thermal dilation of mercury were taken from International Critical Tables. The coefficient of cubical compressibility of mercury was taken to be

$$\beta_{Hg} \times 10^{-6}(\text{atm.}^{-1}) = 3.89 + 5.5 \times 10^{-3}t$$

and the standard density of mercury, 13.59546 gm./ml.

The bulb was considered to extend to − 20 (Fig. 1); the section of capillary from − 20 to + 20 in the region of large thermal gradient was divided into the three parts $i = 1, 2, 3$; and the final length from + 20 to the tip was $i = m$. The point 0 was the top of the thermostat cover. For the highest temperature run in each thermostat, the correction for the length of capillary − 20 to + 20 was checked by computing the correction for the section when divided into 16 parts each 2.5 cm. long, the proper volume and temperature being associated with each length. The maximum error in the correction obtained by division into three parts is less than 5×10^{-4} gm. mercury.

In Table VII are given the values of

$$\Delta M_{wt} = (M_{wt_2} - M_{wt_1})\,\frac{1000}{V_{b0}}$$

the corrected number of grams of mercury (reduced to 1000 ml. basis) that ran out of the bulb when the temperature was increased from t_1 to t_2, the temperatures being given in Column II and the run numbers in Column I. The entries are arranged by increasing temperatures. These values were treated by the method of least squares[3] to obtain the most probable values of m, that is $M_{wt} - M_{w0}$, Red and Green being treated separately. Under the heading obsd.-calcd. are given the deviations of the values of ΔM_{wt} for each bulb from those computed from the corresponding m's. The root-mean-square deviations are 86.01×10^{-4} gm. Hg (39 points) for Red and 114.72×10^{-4} gm. Hg (39 points) for Green. The root-mean-square deviation of ΔM_{wt} for Red and Green taken together from the values computed from the average values of m given in Table VII is 270.49×10^{-4} gm. Hg (78 points).

[3] A. Pérard, Trav. et Mém. Bureau Int., **16,** 77 pp. (1917).

TABLE VII

Calculation of Most Probable Values of m

Deviations are from the values computed from the most probable values of m (one set for Red and one for Green) tabulated at the bottom.

m = most probable mass of mercury (gms.) flowing out of Red (or Green) bulb when heated from 0° to t° C.

α_b (Red)/α_b (Green) = ratio of mean coefficient of thermal dilation of Red to that of Green bulb which would explain the difference in the preceding column.

Run Nos.	Temps.	Red Bulb		Green Bulb		Green-Red
		ΔM_{wt}	Obsd.-calcd.	ΔM_{wt}	Obsd.-calcd.	$\Delta(\Delta M_{wt})$
	°C. Int.	gms. Hg/1000 ml.	gms. Hg × 10^4	gms. Hg/1000 ml.	gms. Hg × 10^4	gm. Hg × 10^4
15–16	0–25	61.0183	− 84	61.0147	−207	− 36
21–22	0–25	61.0206	− 61	61.0294	− 60	+ 88
14–15	0–50	121.6015	− 11	121.5886	−103	− 129
5–6	0–75	181.7779	+111	181.7877	+132	+ 98
6–7	0–100	241.5963	+ 71	241.6075	+ 79	+ 112
20–21	0–152.315	365.9343	− 26	365.9722	+160	+ 379
2–3	25–50	60.5723	− 36	60.5645	+ 10	− 78
16–17	25–50	60.5928	+169	60.5689	+ 54	− 239
9–10	25–75	120.7213	−188	120.7247	−144	+ 34
1–2	25–100	180.5710	+ 85	180.5567	− 75	− 143
10–11	25–152.315	304.8929	−173	304.9097	−111	+ 168
17–18	50–75	60.1737	+ 95	60.1747	− 9	+ 10
3–4	50–100	119.9934	+ 68	119.9992	− 15	+ 58
13–14	50–152.315	244.3299	− 44	244.3556	− 17	+ 257
4–5	75–100	59.8170	− 54	59.8169	− 82	− 1
18–19	75–100	59.8183	− 41	59.8222	− 29	+ 39
8–9	75–152.315	184.1848	+147	184.2035	+218	+ 187
11–12	75–152.315	184.1731	+ 30	184.1754	− 63	+ 23
12–13	75–152.315	184.1635	− 66	184.1751	− 66	+ 116
7–8	100–152.315	124.3550	+ 73	124.3328	−238	− 222
19–20	100–152.315	124.3534	+ 57	124.3679	+113	+ 145
24–25	150–152.315	5.4873	+ 21	5.4893	+ 23	+ 20
25–26	150–152.315	5.4796	− 56	5.4887	+ 17	+ 91
31–32	150–152.315	5.4892	+ 40	5.4928	+ 58	+ 36
32–33	150–152.315	5.4775	− 77	5.4663	−207	− 112
38–39	150–152.315	5.4977	+125	5.4906	+ 36	− 71
39–40	150–152.315	5.4797	− 55	5.4941	+ 71	+ 144
33–34	152.315–200	112.7325	+ 47	112.7498	+229	+ 173
40–41	152.315–200	112.7295	+ 17	112.7334	+ 65	+ 39
37–38	152.315–250	230.6996	− 12	230.7122	+ 25	+ 126
23–24	152.315–300	348.8397	− 26	348.8620	−139	+ 223
26–27	152.315–300	348.8470	+ 47	348.8812	+ 53	+ 342
30–31	152.315–350	467.7777	− 71	467.9224	−232	+1447
28–29	200–250	117.9743	+ 13	117.9902	+ 74	+ 159
34–35	200–300	236.1307	+162	236.1560	+ 70	+ 253
29–30	200–350	355.0458	−112	355.2338	+151	+1880
27–28	250–300	118.1350	− 65	118.1655	− 7	+ 305
36–37	250–350	237.0908	+ 68	237.2466	+107	+1558
35–36	300–350	118.9541	+116	119.0673	− 24	+1132
Root-mean-square deviation			86.01		114.72	513.32[a]
Algebraic average						+ 220.79[a]

Temps. °C. Int.	Most probable values of m (gms. Hg/1000 ml.)				α_b(Red)/α_b(Green)
	Red Bulb	Green Bulb	Average	(Green-Red) × 10^4	
0–25	61.0267	61.0354	61.0310	+ 87	1.0204
0–50	121.6026	121.5989	121.6008	− 37	0.9959
0–75	181.7668	181.7745	181.7706	+ 77	1.0053
0–100	241.5892	241.5996	241.5944	+ 104	1.0052
0–150	360.4517	360.4692	360.4604	+ 175	1.0055
0–152.315	365.9369	365.9562	365.9466	+ 193	1.0059
0–200	478.6647	478.6831	478.6739	+ 184	1.0042
0–250	596.6377	596.6659	596.6518	+ 282	1.0051
0–300	714.7792	714.8321	714.8056	+ 529	1.0079
0–350	833.7217	833.9018	833.8118	+1801	1.0232
Root-mean-square deviation				610.77[b]	
Algebraic average				+ 339.50[b]	

[a] If the four points which involve 350° are omitted 513.32 becomes 163.83 and +220.79 becomes + 74.11.

[b] If the point at 350° is omitted 610.77 becomes 232.56 and +339.50 becomes +177.11.

TABLE VIII

Mean Coefficient of Thermal Dilation of Mercury

$$\alpha_b = 3\alpha_b \text{ (linear)}\,[1 + \alpha_b \text{ (linear)}\, t] \quad [\alpha_b \text{ (linear) from Eq. (A), Table I}].$$

$$\alpha_{Hg} \text{ (apparent)} = \frac{m}{t(M_{b0} - m)}. \qquad [M_{b0} = 13595.46]$$

$$\alpha_{Hg} \text{ (obsd.)} = \alpha_{Hg} \text{ (apparent)} + \frac{M_{b0}\,\alpha_b}{M_{b0} - m}.$$

$$\alpha_{Hg} \times 10^8 \text{ (calcd.)} = 18144.01 + 70.16 \times 10^{-2} t + 28.625 \times 10^{-4} t^2 + 2.617 \times 10^{-6} t^3.$$

$$m \text{ (calcd.)} = \frac{M_{b0}\, t(\alpha_{Hg} - \alpha_b)}{1 + \alpha_{Hg} t}.$$

t	m (0 to t)	$\alpha_b \times 10^8$	α_{Hg} (app.) $\times 10^8$	$\alpha_{Hg} \times 10^8$ (obs.)	$\alpha_{Hg} \times 10^8$ (calcd.)	(Obsd. − calcd.) $\times 10^8$	m (calcd.)	(Obsd. − calcd.) $\times 10^4$
°C. Int.	gm. Hg/ 1000 ml.	°C.$^{-1}$	°C.$^{-1}$	°C.$^{-1}$	°C.$^{-1}$	°C.$^{-1}$	gm. Hg/1000 ml.	gm. Hg/1000 ml.
25	61.0310	125.78	18037.259	18163.606	18163.380	+0.226	61.0302	+ 8
50	121.6008	135.44	18049.884	18186.547	18186.573	−0.026	121.6010	− 2
75	181.7706	143.64	18068.168	18213.755	18213.836	−0.081	181.7714	− 8
100	241.5944	150.54	18091.720	18244.984	18245.412	−0.428	241.6000	− 56
150	360.4604	160.98	18156.928	18322.292	18322.489	−0.197	360.4642	− 38
200	478.6739	167.78	18246.615	18420.518	18419.766	+0.752	478.6549	+190
250	596.6518	171.75	18360.200	18539.834	18539.207	+0.627	596.6323	+195
300	714.8056	173.58	18498.170	18681.383	18682.774	−1.391	714.8565	−509
350	833.8118	173.82	18667.804	18852.981	18852.430	+0.551	833.7887	+231
Root-mean-square deviation*						0.62159		208.51

* Root-mean-square deviations of ΔM_{wt} of Table VII from calculated values are: Red, 331.59 $\times 10^{-4}$ (39 points); Green, 388.64 $\times 10^{-4}$ (39 points); Red and Green, 361.24 $\times 10^{-4}$ (78 points).

It will be noticed (Table VII) that ΔM_{wt} and m are systematically larger for Green than for Red bulb. The root-mean-square deviations are: 513.32×10^{-4} gm. Hg (39 points) for ΔM_{wt} or 163.83×10^{-4} gm. Hg (35 points) if the 350° points are excluded; 610.77×10^{-4} gm. Hg (10 points) for m or 232.56×10^{-4} gm. Hg (9 points) if the 350° point is excluded. The average of the algebraic sum of $\Delta(\Delta M_{wt})$, Green minus Red, is $+ 220.79 \times 10^{-4}$ gm. Hg ($+ 74.11 \times 10^{-4}$ if the 350° points are excluded); and that for Δm, Green minus Red, is $+ 339.50 \times 10^{-4}$ gm. Hg ($+ 177.11 \times 10^{-4}$ if the 350° point is excluded). From Eq. (10)

$$t\Delta\alpha_{Hg} = \Delta m \frac{1 + \alpha_{Hg} t}{M_{b0} - m}, \qquad (13)$$

$$t\Delta\alpha_b = -\Delta m \frac{1 + \alpha_{Hg} t}{M_{b0}}. \qquad (14)$$

The difference between m for Red and for Green bulb can be explained by a difference $\Delta\alpha_{Hg} = 1 \times 10^{-8}$ °C.$^{-1}$ (the 350° point is excluded) where $\alpha_{Hg} \cong 18000 \times 10^{-8}$ °C.$^{-1}$ or a difference $\Delta\alpha_b = -1 \times 10^{-8}$ °C.$^{-1}$ where $\alpha_b \cong 160 \times 10^{-8}$ °C.$^{-1}$ A third cause of this difference would be the presence of a small amount of air in the Green bulb; we believe this to be very improbable. Calculation shows that the presence of a constant amount of air in the bulb would not account for the variation of the difference with temperature.

In the present calculations we shall consider the data taken with Red bulb and Green bulb to be equally accurate and use the mean m. For our gas thermometer calculations we shall take α_b (Red)/α_b (Green) = 1.005.

In Table VIII are given the computations of the mean coefficient of thermal dilation of mercury from the mean values of m of Table VII, the constants of a four-constant equation for α_{Hg} determined by the method of least squares, and the deviations of the calculated from the observed values of α_{Hg} and m. The root-mean-square deviations of the 9 points from the four-constant equation are: $0.621\,59 \times 10^{-8}$ °C.$^{-1}$ for α_{Hg} and 208.51×10^{-4} gm. Hg for m; the corresponding probable errors of a single determination are 0.562×10^{-8} °C.$^{-1}$ for α_{Hg} and 188.7×10^{-4} gm. Hg for m. The root-mean-square deviations of ΔM_{wt} observed (Table VII) from the values computed from the four-constant equation are: 331.59×10^{-4} gm. Hg (39 points) for Red bulb; 388.64×10^{-4} gm. Hg (39 points) for Green bulb; 361.24×10^{-4} gm. Hg (78 points) for Red and Green bulbs. This last value corresponds to a

TABLE IX

COMPARISON OF OUR VALUES OF THE MEAN COEFFICIENT OF THERMAL DILATION OF MERCURY WITH THE RESULTS OF OTHER INVESTIGATORS

$\alpha_{Hg} \times 10^8 = a + bt + ct^2 + dt^3$

Author	Date	a	$b \times 10^4$	$c \times 10^6$	$d \times 10^8$	Range	Bulb
P. T. R. (A)	1895–1919	18182	7800			0–100	16^{III} 59^{III}
P. T. R. (B)	1895–1919	18181	3470	3930	− 20	100–300	59^{III}
Chappuis	1907	18169.041	−2951.266	11456.2		0–100	verre dur
Chappuis	1917	18163.674	+8469.42			0–100	absolute method
Callendar, Moss	1912	18055.53	12444	2539		0–300	absolute method
Sears	1914	18145.6	9205	660.8	+673.20	0–300	vitreous silica
Harlow	1929	18153.8	7548	1533	536	0–300	vitreous silica
This investigation	1940	18144.01	7016	2862.5	261.7	0–350	vitreous silica

Temp., °C. Int.	$\alpha_{Hg} \times 10^8$ °C.$^{-1}$ This investigation	$\Delta\alpha_{Hg} \times 10^8$, other author—our equation									
		P.T.R. (A)	P.T.R. (B)	Chappuis	Chappuis	Callendar, Moss	James*	Harlow*	Sears	Harlow*	Harlow
	1940	1895–1919	1895–1919	1907	1917	1912	1914	1914	1914	1929	1929
25	18163	+39		+6	+22	−75			+ 6		+11
30	18168							0		+ 7	
50	18187	+34		−4	+19	−63		+1	+ 7	+ 5	+ 9
75	18214	+26		−3	+13	−51		−1	+ 7	+ 2	+ 7
100	18245	+15	+10	+9	+ 3	−40	−4	−1	+ 6	+ 2	+ 5
140	18306							−1		− 1	
150	18322		− 1			−23			− 1		− 2
184	18386							+1		− 4	
200	18420		−14			−14		−1	−10	− 8	−11
250	18539		−29			−14		−2	−17	−12	−17
300	18683		−50			−26		−5	−20	−15	−20

* Original data; all other entries are computed from the equations given.

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Sears, Proc. Phys. Soc. London, **26**, 95 (1914).

probable error of 250.2×10^{-4} gm. Hg (78 points) or approximately 0.002 ml. in the volume of mercury run out of a one-liter bulb.

In Table IX the mean coefficients of thermal dilation of mercury computed from our equation are compared with the values of other investigators. The accord of our equation for α_{Hg} with the measurements of Harlow (1914) is astonishingly good, the root-mean-square deviation being 1.97×10^{-8} °C.$^{-1}$ (9 points). In 1929 Harlow recomputed his measurements using the apparent coefficients of dilation determined in 1914 but new values of α_b for vitreous silica obtained from a critical survey of all of the available data (see Table III). Our equation does not agree so well with his 1929 values, the root-mean-square deviation being 7.69×10^{-8} °C.$^{-1}$ (9 points). It is possible that the values of α_b used by Harlow in 1914 which were determined by Callendar (see Table III) with a sample made at the same time that the bulbs were manufactured more nearly represented the thermal dilation of Harlow's bulbs than the values he selected in 1929.

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6. SUMMARY

The apparent mean coefficient of thermal dilation of mercury in each of two one-liter vitreous silica bulbs has been determined for the tempera-

TABLE X

MEAN COEFFICIENT OF THERMAL DILATION OF MERCURY FROM 0° TO t° C.

$$\alpha^\circ \text{C.}^{-1} \text{ (Int.)} \times 10^8 = \frac{V_t - V_0}{tV_0}.$$

$$= 18144.01 + 70.16 \times 10^{-2}t + 28.625 \times 10^{-4}t^2 + 2.617 \times 10^{-6}t^3. \quad (0^\circ < t^\circ \text{ C. (Int.)} < 350^\circ)$$

°C. (Int.)	0	1	2	3	4	5	6	7	8	9
	α° C.$^{-1}$ (Int.) $\times 10^8$									
0	18 144.01	18 144.71	18 145.42	18 146.14	18 146.86	18 147.59	18 148.32	18 149.06	18 149.81	18 150.56
10	151.31	152.08	152.85	153.62	154.40	155.19	155.98	156.78	157.58	158.39
20	159.21	160.03	160.86	161.69	162.53	163.38	164.23	165.09	165.96	166.83
30	167.70	168.59	169.48	170.37	171.28	172.18	173.10	174.02	174.95	175.88
40	176.82	177.77	178.72	179.68	180.65	181.62	182.60	183.58	184.57	185.57
50	186.57	187.58	188.60	189.63	190.66	191.69	192.74	193.79	194.84	195.91
60	196.98	198.05	199.14	200.23	201.32	202.43	203.54	204.65	205.78	206.91
70	208.05	209.19	210.34	211.50	212.66	213.84	215.01	216.20	217.39	218.59
80	219.80	221.01	222.23	223.46	224.69	225.93	227.18	228.44	229.70	230.97
90	232.25	233.53	234.82	236.12	237.43	238.74	240.06	241.39	242.72	244.06
100	245.41									

°C. (Int.)	00	10	20	30	40	50	60	70	80	90
	α° C.$^{-1}$ (Int.) $\times 10^8$									
100	18 245.41	18 259.31	18 273.94	18 289.34	18 305.52	18 322.49	18 340.27	18 358.87	18 378.31	18 398.60
200	419.77	441.82	464.77	488.65	513.45	539.21	565.93	593.63	622.33	652.04
300	682.77	714.56	747.40	781.31	816.32	852.43				

ture range 0° to 350° C. Thirty-nine measurements were made with each bulb.

The thermal expansion of a ring of vitreous silica prepared from one of the bulbs and annealed in the same manner as the bulb was measured at 88 temperatures from − 200° to + 450° C. The results may be represented by the equations:

$$\frac{l - l_0}{l_0} \times 10^6 = \frac{t^2 + 157.361t}{0.00126792t^2 + 0.88121t + 412.109}, \quad -175^\circ < t^\circ\text{C.} < +450^\circ$$

$$\frac{V - V_0}{V_0} \times 10^6 = \frac{t^2 + 157.281t}{0.0004225t^2 + 0.29362t + 137.32}, \quad -175^\circ < t^\circ\text{C.} < +450^\circ$$

where t is on the Centigrade thermodynamic temperature scale when below 0° C. and on the International scale when above 0°, l_0 [V_0] is the length [volume] at 0° C., and l [V] the length [volume] at t°. The probable error of a single determination measured by the deviations of the observed values from those computed from this equation is 0.56×10^{-6} in $(l - l_0)/l_0$ (80 points, 10 series). The temperature of minimum length of the sample was − 84.6° C. The values of the mean coefficient of linear thermal expansion of vitreous silica computed from the equation are in fair agreement with the values selected by Sosman.

From the dilation of the bulbs caused by a difference between internal and external pressure at several temperatures and Horton's values of the rigidity we computed the mean coefficient of compressibility of vitreous silica at low pressures as a function of temperature:

$$\beta \times 10^6 \text{ (atm.}^{-1}) = 2.70 - 6 \times 10^{-4}t, \quad 0^\circ < t^\circ \text{ C.} < 300^\circ$$

where t is in degrees Centigrade. The values computed from the equation are in good agreement with those obtained by the compressibility methods. The values of β for the two bulbs differed about 5%.

The apparent mean thermal dilations of mercury determined in the two bulbs differed systematically by an amount that could be interpreted as a variation in the mean coefficient of thermal dilation of mercury of 1×10^{-8} °C.$^{-1}$ (about 1 part in 18000) or a variation in the mean coefficient of thermal dilation of the vitreous silica of the bulbs of 1×10^{-8} °C.$^{-1}$ (about 1 part in 160). In terms of volume this systematic difference between the results in the one bulb and in the other is on the average 0.002 ml. in 1000 ml. or 2 parts in 10.[6]

We considered the results obtained by use of the two bulbs equally accurate for the present purpose. The equation obtained for the thermal dilation of mercury is

$$\frac{V-V_0}{V_0} \times 10^8 = \alpha_{Hg} t \times 10^8 = 18144.01t + 70.16 \times 10^{-2}t^2 + 28.625 \times 10^{-4}t^3 + 2.617 \times 10^{-6}t^4, \quad 0° < t° \text{ C.} < 350°$$

where t is on the International temperature scale. The probable error of a single determination of α_{Hg} is 0.56×10^{-8} °C.$^{-1}$ (9 points). The above equation agrees well with the 1914 measurements of Harlow, the probable error of a single determination of α_{Hg} being 1.78×10^{-8} °C.$^{-1}$ (9 points).

Values of the following quantities as functions of temperature are tabulated for mercury from 0° to 350° C.: the true and the mean coefficients of thermal dilation, the density and the specific volume, and the ratio of the density at $t°$ to that at 0° C. Tables for the following properties of vitreous silica are given from − 150° to + 450° C.: the true and the mean coefficients of linear thermal expansion and of thermal dilation.

TABLE XI

TRUE COEFFICIENT OF THERMAL DILATION OF MERCURY AT $t°$ REFERRED TO 0° C.

$$\alpha' = \frac{1}{V_0}\frac{dV}{dt} = \frac{d(\alpha t)}{dt}.$$

°C. (Int.)	00	10	20	30	40	50	60	70	80	90
	α'° C.$^{-1}$ (Int.) × 10^8									
0	18 144.01	18 158.91	18 175.59	18 194.12	18 214.55	18 236.95	18 261.38	18 287.90	18 316.59	18 347.49
100	18 380.67	18 416.20	18 454.74	18 494.55	18 537.50	18 583.04	18 631.24	18 682.16	18 735.87	18 792.43
200	18 851.89	18 914.33	18 979.81	19 048.39	19 120.13	19 195.09	19 273.34	19 354.94	19 439.96	19 528.45
300	19 620.48	19 716.11	19 815.41	19 918.43	20 025.25	20 135.91				

TABLE XII

RATIO OF THE DENSITY OF MERCURY AT $t°$ TO THE DENSITY AT 0° C.

$$\frac{\delta_t}{\delta_0} = \frac{V_0}{V_t} = \frac{1}{1+\alpha t}$$

°C. (Int.)	0	1	2	3	4	5	6	7	8	9
	$\delta_t/\delta_0 = V_0/V_t = (1 + \alpha t)^{-1}$									
0	1.0000 0000	0.9998 1859	0.9996 3722	0.9994 5591	0.9992 7465	0.9990 9344	0.9989 1229	0.9987 3118	0.9985 5012	0.9983 6911
10	0.9981 8816	80 0725	78 2639	76 4559	74 6483	72 8412	71 0346	69 2285	67 4228	65 6177
20	63 8130	62 0088	60 2051	58 4019	56 5991	54 7968	52 9950	51 1936	49 3927	47 5923
30	45 7923	43 9928	42 1938	40 3952	38 5970	36 7993	35 0021	33 2053	31 4089	29 6130
40	27 8175	26 0225	24 2279	22 4337	20 6400	18 8467	17 0538	15 2614	13 4694	11 6777
50	09 8866	08 0958	06 3054	04 5155	02 7260	00 9369	.9899 1482	.9897 3598	.9895 5719	.9893 7844
60	.9891 9973	.9890 2106	.9888 4243	.9886 6384	.9884 8529	.9883 0677	81 2830	79 4986	77 7146	75 9310
70	74 1477	72 3649	70 5824	68 8003	67 0185	65 2371	63 4561	61 6755	59 8952	58 1152
80	56 3356	54 5564	52 7775	50 9990	49 2208	47 4430	45 6655	43 8883	42 1115	40 3350
90	38 5589	36 7830	35 0075	33 2324	31 4575	29 6830	27 9088	26 1349	24 3614	22 5881
100	20 8152									

°C. (Int.)	00	10	20	30	40	50	60	70	80	90
	$\delta_t/\delta_0 = V_0/V_t = (1 + \alpha t)^{-1}$									
100	0.9820 8152	0.9803 1024	0.9785 4182	0.9767 7603	0.9750 1264	0.9732 5142	0.9714 9212	0.9697 3452	0.9679 7836	0.9662 2340
200	.9644 6940	.9627 1611	.9609 6327	.9592 1064	.9574 5796	.9557 0497	.9539 5142	.9521 9705	.9504 4159	.9486 8478
300	.9469 2637	.9451 6608	.9434 0364	.9416 3880	.9398 7128	.9381 0082				

TABLE XIII

Density of Mercury at t° C.

$$\delta_t \text{ (gm./ml.)} = \frac{\delta_0}{1 + \alpha t} = \frac{13.59546}{1 + \alpha t}.$$

°C. (Int.)	0	1	2	3	4	5	6	7	8	9
	Density, gm./ml.									
0	13.59 546	13.59 299	13.59 053	13.58 806	13.58 560	13.58 313	13.58 067	13.57 821	13.57 575	13.57 329
10	.57 083	.56 837	.56 591	.56 345	.56 099	.55 854	.55 608	.55 362	.55 117	.54 872
20	.54 626	.54 381	.54 136	.53 891	.53 645	.53 400	.53 155	.52 911	.52 666	.52 421
30	.52 176	.51 932	.51 687	.51 442	.51 198	.50 954	.50 709	.50 465	.50 221	.49 977
40	.49 732	.49 488	.49 244	.49 001	.48 757	.48 513	.48 269	.48 025	.47 782	.47 538
50	.47 295	.47 051	.46 808	.46 564	.46 321	.46 078	.45 835	.45 592	.45 349	.45 106
60	.44 863	.44 620	.44 377	.44 134	.43 891	.43 649	.43 406	.43 163	.42 921	.42 678
70	.42 436	.42 193	.41 951	.41 709	.41 467	.41 224	.40 982	.40 740	.40 498	.40 256
80	.40 014	.39 772	.39 530	.39 289	.39 047	.38 805	.38 564	.38 322	.38 080	.37 839
90	.37 597	.37 356	.37 115	.36 873	.36 632	.36 391	.36 149	.35 908	.35 667	.35 426
100	.35 185									
°C. (Int.)	00	10	20	30	40	50	60	70	80	90
	Density, gm./ml.									
100	13.35 185	13.32 777	13.30 373	13.27 972	13.25 575	13.23 180	13.20 788	13.18 399	13.16 011	13.13 625
200	.11 241	.08 857	.06 474	.04 091	.01 708	12.99 325	12.96 941	12.94 556	12.92 169	12.89 781
300	12.87 390	12.84 997	12.82 601	12.80 201	12.77 798	.75 391				

TABLE XIV

Volume of Unit Mass of Mercury at t° C.

$$V_t \text{ (ml./gm.)} = V_0 (1 + \alpha t) = \frac{1 + \alpha t}{13.59546}.$$

°C. (Int.)	0	1	2	3	4	5	6	7	8	9
	Volume, ml./gm.									
0	0.073 5540	0.073 5673	0.073 5807	0.073 5940	0.073 6074	0.073 6207	0.073 6341	0.073 6474	0.073 6608	0.073 6741
10	6875	7008	7142	7276	7409	7543	7676	7810	7944	8077
20	8211	8345	8478	8612	8746	8880	9013	9147	9281	9415
30	9549	9682	9816	9950	.074 0084	.074 0218	.074 0352	.074 0486	.074 0620	.074 0754
40	.074 0888	.074 1022	.074 1156	.074 1290	1424	1558	1692	1826	1960	2094
50	2228	2362	2496	2631	2765	2899	3033	3168	3302	3436
60	3570	3705	3839	3973	4108	4242	4377	4511	4646	4780
70	4915	5049	5184	5318	5453	5587	5722	5857	5991	6126
80	6261	6396	6530	6665	6800	6935	7070	7204	7339	7474
90	7609	7744	7879	8014	8149	8284	8419	8554	8690	8825
100	8960									
°C. (Int.)	00	10	20	30	40	50	60	70	80	90
	Volume, ml./gm.									
100	0.074 8960	0.075 0313	0.075 1669	0.075 3028	0.075 4390	0.075 5755	0.075 7124	0.075 8496	0.075 9872	0.076 1252
200	.076 2637	.076 4026	.076 5419	.076 6818	.076 8221	.076 9630	.077 1045	.077 2466	.077 3893	.077 5326
300	.077 6765	.077 8212	.077 9666	.078 1127	.078 2596	.078 4073				

TABLE XV

MEAN COEFFICIENT OF THERMAL DILATION OF VITREOUS SILICA FROM 0° TO t °C.

$$\alpha\ °C.^{-1} \times 10^8 = \frac{V_t - V_0}{tV_0} \times 10^8.$$

$$= \frac{100\,(t + 157.281)}{0.0004225t^2 + 0.29362t + 137.32}. \qquad \begin{matrix}(-150° < t\ °C.\ (\text{thermodynamic}) < 0°)\\ (0° < t\ °C.\ (\text{International}) < +450°)\end{matrix}$$

°C.	00	10	20	30	40	50	60	70	80	90
	$\alpha\ °C.^{-1} \times 10^8$									
−100	51.06	42.93	34.47	25.67	16.54	7.08				
− 0	114.54	109.56	104.30	98.75	92.89	86.73	80.25̄	73.45̄	66.32	58.86
+ 0	114.54	119.23	123.66	127.83	131.75̄	135.43	138.87	142.10	145.11	147.92
+100	150.54	152.97	155.22	157.30	159.22	160.99	162.61	164.10	165.45̄	166.67
200	167.78	168.78	169.67	170.46	171.15̄	171.75	172.27	172.71	173.07	173.36
300	173.59	173.75̄	173.85̄	173.89	173.88	173.82	173.71	173.56	173.37	173.14
400	172.87	172.57	172.24	171.87	171.48	171.06				

TABLE XVI

TRUE COEFFICIENT OF THERMAL DILATION OF VITREOUS SILICA AT $t°$ REFERRED TO 0 °C.

$$\alpha' = \frac{1}{V_0}\frac{dV}{dt} = \frac{d(\alpha t)}{dt}.$$

°C.	00	10	20	30	40	50	60	70	80	90
	$\alpha'\ °C.^{-1} \times 10^8$									
−100	− 28.56	− 48.34	− 69.12	− 90.87	−113.56	−137.13				
− 0	+114.54	+104.45̄	+ 93.49	+ 81.64	+ 68.86	+ 55.12	+ 40.40	+ 24.69	+ 7.96	− 9.79
+ 0	114.54	123.79	132.25	139.96	146.94	153.24	158.89	163.93	168.39	+172.32
+100	175.74	178.70	181.21	183.31	185.03	186.39	187.43	188.17	188.63	188.83
200	188.80	188.55	188.11	187.49	186.70	185.76	184.69	183.50̄	182.20	180.80
300	179.31	177.75̄	176.12	174.42	172.68	170.89	169.06	167.20	165.31	163.40
400	161.47	159.53	157.58	155.62	153.66	151.70				

TABLE XVII

MEAN COEFFICIENT OF LINEAR THERMAL EXPANSION OF VITREOUS SILICA FROM 0° TO t °C.

$$\alpha_{\text{linear}}\ °C.^{-1} \times 10^8 = \frac{l_t - l_0}{t\,l_0} \times 10^8.$$

$$= \frac{100\,(t + 157.361)}{0.00126792t^2 + 0.88121t + 412.109}. \qquad \begin{matrix}(-150° < t\ °C.\ (\text{thermodynamic}) < 0°)\\ (0° < t\ °C.\ (\text{International}) < +450°)\end{matrix}$$

°C.	00	10	20	30	40	50	60	70	80	90
	$\alpha_{\text{linear}}\ °C.^{-1} \times 10^8$									
−100	17.04	14.33	11.51	8.58	5.54	2.39				
− 0	38.18	36.53	34.78	32.93	30.98	28.92	26.76	24.50̄	22.12	19.63
+ 0	38.18	39.75̄	41.22	42.61	43.92	45.14	46.29	47.37	48.37	49.31
+100	50.18	50.99	51.74	52.43	53.07	53.66	54.20	54.69	55.14	55.55
200	55.92	56.25	56.55	56.81	57.04	57.24	57.41	57.56	57.68	57.78
300	57.85	57.90	57.94	57.95	57.95̄	57.93	57.89	57.84	57.78	57.70
400	57.61	57.51	57.40	57.28	57.15̄	57.01				

TABLE XVIII

TRUE COEFFICIENT OF LINEAR THERMAL EXPANSION OF VITREOUS SILICA AT $t°$ REFERRED TO 0° C.

$$\alpha'_{\text{linear}} = \frac{1}{l_0}\frac{dl}{dt} = \frac{d\ (\alpha_{\text{linear}}\ t)}{dt}.$$

°C.	00	10	20	30	40	50	60	70	80	90
	α'_{linear} °C.$^{-1}$ × 10^8									
−100	− 9.49	−16.08	−23.00	−30.2$\bar{5}$	−37.81	−45.66				
− 0	+38.18	+34.82	+31.17	+27.23	+22.97	+18.39	+13.49	+ 8.25	+ 2.68	− 3.24
+ 0	38.18	41.27	44.09	46.65	48.98	51.08	52.96	54.64	56.12	+57.43
+100	58.57	59.55	60.39	61.09	61.66	62.12	62.46	62.71	62.86	62.93
200	62.92	62.83	62.69	62.48	62.22	61.90	61.5$\bar{5}$	61.1$\bar{5}$	60.71	60.2$\bar{5}$
300	59.75	59.23	58.69	58.12	57.54	56.94	56.34	55.71	55.09	54.4$\bar{5}$
400	53.81	53.16	52.51	51.86	51.20	50.55				

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 477)

AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE

IX. THE DETERMINATION OF THE CAPILLARY DEPRESSION AND MENISCUS VOLUME OF MERCURY IN A MANOMETER

By James A. Beattie, B. Edwin Blaisdell, and Joseph Kaye

TABLE OF CONTENTS

1. Introduction 389
2. Determination of the Bore of Manometer Tubes 390
3. Determination of the Elevations of the Crown and Bottom of a Mercury Meniscus 390
4. Determination of the Capillary Constant of Mercury 393
(a) From Measurement of Meniscus Volumes 393
(b) Method of Eötvös 394
(c) X-ray Shadowgraph Method 395
5. Summary 397

1. Introduction

In precise gas thermometric investigations two of the significant factors entering into the reduction of the data are: (1) the capillary depression correction, that is, the difference between the capillary depression of mercury in the long and short arms of the manometer, and (2) the dead space correction for the co-volume of the mercury meniscus, that is, the correction for the temperature and variation of the volume of the gas below a horizontal plane tangent to the crown of the meniscus in the short arm (the volume of a cylinder of height equal to that of the meniscus and diameter equal to the bore of the manometer tube minus the volume of the meniscus). The capillary depression and the volume of the meniscus may be expressed in terms of the following quantities which can be determined experimentally: (1) the bore of the manometer tube, (2) the height of the meniscus, and (3) the capillary constant of mercury. The present paper deals with methods of measurement of the bore of the tube, the elevations of the crown and bottom of the meniscus, and the determination of the capillary constant of mercury in situ.

Since capillary depression decreases and meniscus covolume increases with increasing bore of tube, the selection of the manometer tube represents a compromise. Most investigators[1] have used tubes between 1.5 and 2.0 cm. bore.

Let δ_1 be the capillary depression in the long arm of the manometer and δ_2 the depression in the short arm. The capillary depression correction is $\delta_1 - \delta_2$. In general the long arm of the manometer is evacuated so that the height of meniscus and δ is less than in the short arm which contains the thermometric gas. For tubes of 2.0 cm. bore, δ_1 and δ_2 are each of the order of 0.04 mm., $\delta_1 - \delta_2$ of the order of 0.01 mm., and the maximum variation from the least to the greatest value of $\delta_1 - \delta_2$ is about 0.005 mm.; where the capillary constant for mercury is taken to be 0.266 cm. The reported measurements[2] on capillary depressions are not in agreement due probably to differences in the capillary constant of the mercury used. A small amount of impurity has a relatively large effect on the value of the constant.

The correction δ_5 to be added to the observed pressure p' for the variation ΔV_c in the meniscus covolume V_c from some arbitrarily selected standard value (so chosen that ΔV_c is always positive) is

$$\delta_5 = p' \frac{\Delta V_c}{V},$$

where V is the total volume (bulb and dead space) of the gas thermometer at standard con-

[1] For a description of our gas thermometer system and a list of references to the apparatus of other investigators see J. A. Beattie, D. D. Jacobus, J. M. Gaines, Jr., M. Benedict, and B. E. Blaisdell, Proc. Am. Acad. Arts Sci., **74**, 327–342 (1941).

[2] W. Heuse, Z. Instr., **47**, 324 (1927); W. Cawood and H. S. Patterson, Trans. Faraday Soc., **29**, 514–523 (1933).

ditions; and the correction $\mathfrak{E}_6$ for the deviation of the Kelvin temperature T_c of the gas in the covolume from that T_b of the bulb is

$$\mathfrak{E}_6 = p' \frac{V_c}{V}\left(\frac{T_b}{T_c} - 1\right).$$

For tubes of 2.0 cm. bore V_c is of the order of 0.15 ml. and the maximum value of ΔV_c is about 0.02 ml. When $p' = 1366$ mm., $V = 1000$ ml., $T_b = 373$, and $T_c = 298$, $\mathfrak{E}_5$ is about 0.03 mm. and $\mathfrak{E}_6$ about 0.05 mm. The measurements of the volumes of mercury menisci by Scheele and Heuse[3] and by Keesom, van der Horst, and Taconis[3] agree to about 1%, while those by Palacios[3] differ from the average of these by approximately 5%.

In the past it has been the usual practice to omit the capillary depression correction or to determine it from tables[4] expressing the correction as a function of tube bore and meniscus height. The covolume of the meniscus was generally assumed to be constant or to be given by one of the published tables. Keesom, van der Horst, and Taconis[5] determined the meniscus volume at each gas thermometer measurement from an X-ray shadowgraph of the meniscus, the volume being computed as the sum of a number of spherical segments whose dimensions were derived from measurements of the plate. This gives the correct covolume for each measurement independent of any assumption concerning the capillary constant of mercury.

In our measurements we determined: the bore of the manometer tubes, the meniscus height for each measurement, and the capillary constant of the mercury in the manometer. The methods employed for determining each quantity are described in the present paper. The tables of the properties of menisci that we used have been prepared[6] by numerical integration of Laplace's differential equation for the equilibrium meridian of a fluid drop of axial symmetry in a gravitational field.

2. Determination of the Bore of Manometer Tubes

The bore of the short arm just below the index and that of the long arm at various heights should be measured after the tubes are in place. The former affects the value of meniscus covolume read from the tables as well as the computed capillary depression correction and should be known more accurately than the latter. The methods found feasible are:

(a) The measurement of the diameter of the image of the mercury column on photographic plates taken with X-rays. This is described in a later section of the present paper.

(b) The determination of the volume (from mass and temperature) and length of a column of mercury about 0.5 cm. high which was run out of the tube into a weighing bottle. Meniscus heights were measured before and after the mercury was run out and correction made for the difference in meniscus volumes.

(c) The determination of the volume (from a calibrated mercury injector[1]) and length of a column of mercury about 0.5 cm. high withdrawn into the injector, correction being made for meniscus volumes.

In all calibrations mercury was always drawn or forced into the manometer tubes from the bottom and the tubes were evacuated during filling. During the measurements the tubes were filled with nitrogen or air to one atmosphere pressure. The tubes were shaken before and after withdrawal of mercury so that meniscus heights were approximately the same at each reading.

All three methods agreed on the diameter of 2.0 cm. bore tubes to $\pm$ 0.1%. An error of 0.1% in the bore introduces an error of 2×10^{-4} mm. in the computation of the capillary depression and 2×10^{-4} ml. in the covolume of the meniscus.

3. Determination of the Elevations of the Crown and Bottom of a Mercury Meniscus

When only a few pressures are to be read and the approximate positions of the mercury meniscus in the long arm of the manometer are known, glass fibers[7] or platinum wires[8] may be sealed in

[3] K. Scheel and W. Heuse, Ann. der Physik, (4) **33,** 291–295 (1910); W. H. Keesom, Miss H. van der Horst, and K. W. Taconis, Kamerlingh Onnes Lab., Univ. of Leiden, Comm. No. **248a,** 5 pp. (1937); J. Palacios, Physik. Z., **24,** 151–155 (1923).

[4] In some cases the tables were prepared from the equation of T. Lohnstein, Ann. der Physik, (4) **33,** 296–307 (1910). For the capillary constant of mercury the value 0.25 cm. was usually used.

[5] W. H. Keesom, Miss H. van der Horst, and K. W. Taconis, Kamerlingh Onnes Lab., Univ. of Leiden, Comm. No. **230d,** 9 pp. (1933–4); see also Comm. No. **248a,** 5 pp. (1937).

[6] B. E. Blaisdell, J. Math. Phys., **19,** 186–245 (1940).

[7] J. T. Howarth and F. B. Burt, Trans. Faraday Soc., **20,** 544–549 (1924).

[8] W. Heuse and J. Otto, Ann. der Physik (5) **2,** 1012–1030 (1929).

with their bent-down points at the desired positions and the mercury brought into optical contact with the point by a slight adjustment of the dead space volume. We have not used this method.

When elevations are read by means of a vertical comparator and scale hung at the same optical distance from the objective of the telescope as the axis of the manometer tubes, the method of illumination of the meniscus has an important effect on the apparent elevation of the crown or bottom.

Four methods of illumination of the crown have been studied. In all investigations the room was darkened and the only source of light was in back of the manometer tubes. The methods are:

(1) Diffuse light coming from behind the manometer and a paper having diagonal black rulings placed immediately behind the tube.[9] This method has been found to be unsatisfactory for precision work.[10]

(2) Diffuse light coming from behind the manometer and a shield shaped to fit the back half of the manometer tube, the bottom of the shield[11] being a fixed distance above the crown of the meniscus thus forming a horizontal slit. The apparent elevation of the crown is a function of the height of the slit.[12]

(3) Parallel light,[5] produced by a spherical lens with a small illuminated disk at its principal focus, coming from behind the meniscus, with or without a shield. The apparent elevation of the crown is independent of slit width but the lens effect of the manometer tube causes some difficulties.[12]

(4) Light[11] that behaves as parallel light in vertical planes and as diffuse light in horizontal planes, produced by a cylindrical lens placed with its elements horizontal and an illuminated slit at its principal focus, coming from behind the manometer, with or without a shield. The apparent elevation of the crown of a meniscus read with this method of illumination is independent[12] of: the relative elevation of the axis of the telescope and the crown provided the telescope is focused on the axis of the manometer tubes, vertical displacement and variation in zenith angle of the optical system provided the beam of light does not slope downward, lateral displacement and variation in azimuthal angle of the optical system, and slit height.

With the last method of illumination which is the most satisfactory so far investigated the image of the meniscus viewed through the eyepiece of the telescope is inverted and a dead black shadow against a light background. The cross-hair in the telescope was elevated by turning the micrometer screw until a narrow band of light, perhaps 0.005 mm. high at the center, remained visible above its upper edge. An experienced observer remembers the width of this band and is able to set the cross-hair on the meniscus with a probable error of a single observation of 0.001 mm. (5 readings).

Two methods of illumination of the bottom of the meniscus have been employed.

(a) Method (4) described above. With this type of illumination the glass tube surrounding the mercury column appears to an observer dark where mercury touches the glass and light where no mercury touches, these regions being separated by fine intensely black horizontal lines, one on each side of the tube, in the plane of the circle of contact of the mercury with the glass, that is, in the plane of the bottom of the meniscus. The cross-hair in the telescope was set on the crown of the meniscus and on the right and left black lines in the glass so that the height of the narrow band of light remaining visible above its upper edge was the same in each case. The mean of the micrometer readings when the hair-line was set on the right and left black lines was taken to be the elevation of the bottom of the meniscus. An experienced observer can read the height of a meniscus—micrometer reading for setting on crown minus mean reading for bottom—by the means just described, Method (4, a), with a probable error of 0.003 mm. (5 readings). The variation of the experimental conditions mentioned above under Method (4) produces no effect on the observed height.

(b) When the magnification of the eyepiece of the telescope is too great to permit viewing the entire meniscus without rotation of the bar of the comparator we read the bottom of the meniscus with diffuse illumination from in front of the manometer tube. A piece of frosted glass 2 cm. high by 1 cm. wide placed vertically was lighted from behind by a small flashlight bulb enclosed in a light-tight box. The window faced the manometer tube and its center was in the same

[9] W. C. Röntgen, Pogg. Ann. der Physik, **148,** 580–624 (1873).

[10] S. C. Collins and B. E. Blaisdell, Rev. Sci. Instr., **7,** 359 (1936).

[11] See Fig. 4, ref. 1.

[12] S. C. Collins and B. E. Blaisdell, Rev. Sci. Instr., **7,** 213–214 (1936).

horizontal plane as the bottom of the meniscus, about 16 cm. in front of the axis of the manometer tube but displaced laterally about 2 cm. from the axis of the telescope so as to be just outside of the field of view. With this method of illumination an observer sees in the upper part of the field of view of the telescope a broad band of bright light one or more millimeters wide against a dark background where the mercury touches the glass tube and acts as a vertically placed cylindrical mirror. The bright band tapers at its bottom, being trapezoidal in form for the lower 0.3 millimeter or so, and is continued downward as a much less intense band of light caused by reflection from the glass surfaces. The bottom edge of the trapezoid, which separates the bright and the less intense portions of the band, is a fairly narrow dark, but not black, horizontal line. The cross-hair in the telescope was elevated until its upper edge coincided with the bottom of the bright band of light. There was thus a lack of symmetry in the setting of the cross-hair on the crown and on the bottom of the meniscus and this could not be overcome since the crown appeared dark against a light background and we moved the hair-line up until a narrow band of light remained between the top of the cross-hair and the shadow of the meniscus, while the bottom of the bright band appeared light against a darker background and we moved the hair-line up until its top edge coincided with the bottom of the bright band. For a fixed position of meniscus and telescope an experienced observer could read the height of a meniscus by this method of illumination, Method (4, b), with a probable error of 0.005 mm. (5 readings). However the apparent height depended on the relative elevations of the bottom of the meniscus and the axis of the telescope.

Since the telescope was in focus for the axis of the manometer tube it was out of focus for the front point of the bottom of the meniscus by a distance equal to the radius of the manometer tube so that the image of the band of light reflected from the cylindrical column of mercury was in a vertical plane farther away from the objective than the plane of the cross-hair; the image of the crown of the meniscus was of course in the plane of the cross-hair. The observed elevation of the bottom of the meniscus was in error; that of the crown, correct.

Let:

h = true height of meniscus determined by Method (4, a).

h' = apparent height determined by Method (4, b).

r = internal radius of manometer tube.

d = horizontal distance from first principal plane of the objective to axis of manometer tube, the image of an object in the axis being in the vertical plane of the cross-hair.

δ = vertical distance from the axis of the telescope to a horizontal plane through the bottom of the meniscus, positive if the plane is below the axis, negative if above.

Δ = radius of the entrance pupil of the telescope (the objective).

ε = error due to lack of symmetry of setting of cross-hair on the crown and bottom of the meniscus.

If we interpret the apparent bottom of the trapezoid of the bright band of light seen in the telescope as being the line of intersection with the vertical plane of the hair-line of the rays of light that are reflected from the top edge of the cylinder of mercury and pass through the lowest point of the objective, we obtain:

$$h = h' - \frac{r}{d-r}\delta + \frac{r}{d-r}\Delta - \varepsilon, \qquad (1)$$

where the second term on the right side of the equation is the correction for the magnification of the distance from the axis of the telescope to the bottom of the meniscus, the third term that for the circle of confusion determined by the ray of light from the bottom of the meniscus that passes through the lowest point of the objective, and the fourth that for the lack of symmetry of setting the hair-line on the crown and bottom of the meniscus. The last two effects cannot be separated since we do not know exactly where within the circle of confusion the hair-line is set, even though the setting can be made reproducibly. For a given observer and apparatus in which the only variable is δ, Eq. (1) may be written:

$$h = h' - \frac{r}{d-r}\delta' + \Delta', \qquad (2)$$

where δ' is the apparent value of δ as measured in the telescope by Method (b) illumination—micrometer reading when hair-line is set on bottom of bright band of light minus reading when set on axis of telescope—and Δ' is an empirical constant (positive or negative) to be determined experimentally by measurement of the apparent height h' of some one meniscus for a series of values of δ' and determination of the

true height by the Method (4, a) or from an X-ray shadowgraph.

For a manometer tube of 2 cm. bore the axis of which was 62.3 cm. distant from the telescope objective we found in one instance:

$$h = h' - .0163\delta' - .004 \qquad (3)$$

for h, h', and δ' in mm. Thus for this observer and experimental equipment the correction to the observed height h' of the meniscus was $-.004$ mm. for $\delta' = 0$, -0.037 mm. for $\delta' = 2$ mm., and -0.069 mm. for $\delta' = 4$ mm. In other circumstances quite different values of Δ' were obtained, the value being sometimes positive.

4. Determination of the Capillary Constant of Mercury

Consider a glass tube with its axis vertical containing mercury. Let:

r = radius (cm.) of the tube.

h = height (cm.) of the mercury meniscus.

h_0 = capillary depression (cm.) of the mercury in the tube.

x, y = Cartesian coördinates (cm.) of a point on the surface of the meniscus; the origin is at the intersection of the axis of the manometer tube with the surface of the meniscus, y is the vertical distance (measured downward along the axis) to a horizontal plane passing through the point in question, and x is the radial distance measured in this plane from the axis to the point. When the point is in the bottom of the meniscus, $y = h$ and $x = r$.

ϕ = angle made by a tangent to the meniscus in the meridian plane with the horizontal.

v = volume (cm.^{3}) of the meniscus above a horizontal plane through the bottom.

a = capillary constant (cm.) of mercury.

$$H_0 \equiv \frac{h_0}{a}\,;\; X \equiv \frac{x}{a}\,;\; Y \equiv \frac{y}{a}\,;\; V \equiv \frac{v}{a^3}\,;$$

these four quantities being dimensionless ratios.

Tables[6] have been published listing:

I : $\tan\phi$ (or $\cot\phi$) as a function of H_0 and Y (Blaisdell's Tables II and III; pp. 204–207),

II : X as a function of H_0 and Y (Blaisdell's Table IV, pp. 208–211),

III : Y as a function of H_0 and X (Blaisdell's Table V, pp. 212–213),

IV : H_0 as a function of X and Y (Blaisdell's Table I, pp. 218–221),

V : V as a function of X and Y (Blaisdell's Table II, pp. 222–225).

We shall designate these tables by the Roman numerals I to V given at the left.

From these tables the value of the capillary constant a of mercury in a manometer may be determined by three independent methods which involve only observations that can be made on the system in situ.

When the value of a is known we can by multiplication convert Tables IV and V to express:

h_0 as a function of h and r,

v as a function of h and r,

for the mercury in the manometer. By inverse interpolation h_0 and v can be expressed for integer values of the arguments h and r.

Tables expressing h_0 and v as functions of h and r for various values of a will be published shortly. When a is known for the mercury in a manometer these tables will afford a simple means of finding h_0 and v corresponding to measured values of h and r.

(a) *From Measurement of Meniscus Volumes*

The quantities r, v, and h are measured and used to compute a from Table V in which values of the function V ($= v/a^3$) are tabulated, the rows being for constant values of the argument X ($= r/a$) and the columns for constant Y ($= h/a$).

Experimental. The radius of the manometer tube was measured.

A low meniscus was produced by withdrawal of mercury into the calibrated injector[1] and its height h_1 measured. Sufficient mercury was injected to increase the meniscus height 0.05 to 0.10 mm.; and the volume $v_2 - v_1$ of mercury introduced and the height h_2 of the meniscus measured. The experiment was continued until the elevation of the bottom of the meniscus changed, indicating that slipping had occurred.

The measured quantities are thus: r, h_i, Δv_i ($= v_i - v_1$) ($i = 1, 2, \ldots n$) where v_1 is unknown.

Calculations. 1. Select the row X' in Table V having the value of the argument closest to r/a where a is an assumed value (say 0.260 cm.) for the capillary constant of mercury. Compute from the experimental data:

$$a' = r/X',$$

$$Y_i' \text{ (obs.)} = h_i/a', \qquad (i = 1, 2, \ldots n)$$

Compute from row X' of Table V:

V_i' (calcd.) corresponding to Y_i' (obs.) (by direct interpolation), $(i = 1, 2, \ldots n)$

$$\Delta v_i' \text{ (calcd.)} = a'^3\,[V_i' \text{ (calcd.)} - V_1' \text{ (calcd.)}] \qquad (i = 2, 3, \ldots n)$$

$$\nu_i = \Delta v_i \text{ (obs.)} - \Delta v_i' \text{ (calcd.)}, \; (i = 2, 3, \ldots n)$$

$$\Sigma_i\,|\nu_i|$$

2. Repeat the Process 1 using the same experimental data—r, h_i, Δr_i—but the rows X'', X''', etc. of Table V immediately above and below X', thus obtaining the values a'', a''', etc., and the corresponding sums $\Sigma_i|\nu_i''|$, $\Sigma_i|\nu_i'''|$, etc. of the absolute values of the deviations.

Plot $\Sigma_i|\nu_i|$ as ordinate against a as abscissa or express $\Sigma_i|\nu_i|$ as a quadratic function of a. The value of a for the minimum $\Sigma_i|\nu_i|$ is the capillary constant of mercury in the manometer.

Accuracy. This method gave values of a with a probable error of 5% (5 complete sets of observations). The value of a agreed with that determined from the X-ray shadowgraph method within the probable error.

This method is the least accurate of the three described in this paper; but it is the simplest from the viewpoint of both experimental work and computation. The calculation tends to eliminate any error caused by differences in the methods of reading the elevations of the crown and bottom of the meniscus.

In ground and polished glass tubes a high meniscus cannot be obtained so that the possible variation of h is limited and consequently the precision of the method is decreased.

(b) *Method of Eötvös*

In the method of Eötvös[13] the quantities ϕ and y are determined for a mercury meniscus by an optical method and h_0 computed from h and r. These quantities are used to compute a from Table I in which values of the function tan ϕ (or cot ϕ) are tabulated, the rows being for constant values of the argument H_0 ($= h_0/a$) and the columns for constant Y ($= y/a$). The computations are simplified by the fact that tan ϕ varies only slowly with H_0. Since H_0 cannot be measured directly there is obtained from Table IV by interpolation a provisional value; this being the value of the function H_0 for the arguments X ($= r/a$) and Y ($= h/a$). The latter are computed from the radius r of the manometer tube, the height h of the meniscus, and an assumed value of a.

Experimental. The lower half of the objective of the telescope was covered with black paper up to a horizontal line 1 mm. below the axis. The telescope was leveled and set so that the image of the crown of the meniscus was on the axis of the telescope and in the vertical plane of the cross-hair.

The illuminating system for the measurements made by the Eötvös method consisted of a 100-watt bulb enclosed in a box 15 cm. wide. The bottom and the front of the box were covered with translucent paper to produce a source of diffuse light. The upper portion of the paper covering the front was made opaque with black ink. The box was placed behind the manometer with the front facing the telescope so as to illuminate the meniscus by diffuse light coming from behind and with the bottom edge of the opaque portion of the front cover horizontal. The box could be raised or lowered vertically and its front cover was a distance B (large in comparison with the radius of the manometer tube, say 100 cm.) behind the axis of the tube. The distance C from the crown of the meniscus to the bottom edge of the blackened portion of the front was varied from about 25 to 125 cm. in increments of 5 or 10 cm. Viewed through the telescope, a meniscus illuminated in this manner appeared very similar to one illuminated by Method (2) described in an earlier section of this paper, that is, black against a light background. The portion of the meniscus reflecting light into the telescope was invisible or practically invisible against the background of diffuse light coming from the bottom of the light-box. The apparent crown of a meniscus so illuminated is interpreted as the point P on the meniscus and in the plane defined by the axes of the manometer tube and the telescope at which light from the highest point of the front of the light-box (a point just below the bottom of the blackened portion) was reflected horizontally into the telescope. Actually some light was reflected into the telescope from a point slightly below P (about .001 mm. below P for a tube of 1 cm. radius) since the objective was not covered all the way to the axis; but the sharpness of the edges of the shadow of the meniscus indicates that the amount of light reflected into the telescope decreased rapidly below some point which we took to be the point P. The smallest value of the distance C was so chosen that P was about three quarters of the distance from the axis to the inside wall of the manometer tube.

The radius r of the manometer tube was measured.

A stable meniscus was produced by shaking the tube and its true height h measured by Method (4, a) described above. Let P_0 be the true elevation of the crown determined by this method of illumination.

[13] F. Eötvös, Wied. Ann. der Physik, **27,** 448–459 (1886).

The apparent elevation of the crown, that is, the elevation of the point P_1, was measured by use of the illuminating device just described with the bottom of the blackened portion of the paper covering the front of the light-box at a height C_1 above the crown. The process was repeated for a series of values of C. The shape of the meniscus must not change throughout the entire series of observations.

The measured quantities are thus: r, h, B, C_i and P_i $(i = 1, 2, \ldots n)$.

Calculations. From r, h, and a provisional value of a (say 0.260 cm.) compute $X\ (= r/a)$ and $Y\ (= h/a)$ and read from Table IV the corresponding provisional value of the function H_0. *All of the computations* described below are made by use of the row H_0 for which the value of the argument H_0 is nearest the provisional value.

1. In order to calculate y_i and ϕ_i we must know the x_i coordinate of the point P_i. From row H_0 of Table II compute by interpolation the value of the function X_i for the argument $Y_i\ [= (P_0 - P_i)/a]$ and hence find $x_i\ (= X_i a)$ for the points $i = 1, 2, \ldots n$.

Now compute the value of y_i by Eq. (1):

$$y_i = (P_0 - P_i) - \frac{x_i}{d - x_i}(P_0 - P_i), \qquad (i = 1, 2, \ldots n) \quad (4)$$

where Δ and ε have been set equal to zero. Compute ϕ_i from the relation:

$$\phi_i = \frac{1}{2}\tan^{-1}\frac{C_i + y_i}{B_i + x_i}, \qquad (i = 1, 2, \ldots n) \quad (5)$$

and read $\tan \phi_i$ from trigonometric tables.

From row H_0 of Table I compute:

Y_i (calcd.) corresponding to $\tan \phi_i$ (by inverse interpolation). $(i = 1, 2, \ldots n)$.

By the method of least squares express y_i as a linear function of Y_i (calcd.). The slope dy_i/dY_i (calcd.) is a.

2. If the calculated value of a is greatly different from the provisional value used to compute H_0, repeat Process (1) using the value just obtained for evaluating a new H_0.

Accuracy. This method gave values of a with a probable error of 1.5% (5 sets of measurements) for mercury in a manometer tube of 2 cm. bore. The mean agreed with the value of a given by the X-ray shadowgraph method within the probable errors of the two methods.

We computed a from one set of measurements for mercury in a tube of 2 cm. bore using as provisional values 0.260 and 0.255 cm. for a and using the rows 0.010 and 0.009 for H_0 with each provisional a. The total spread of the calculated values of a was 0.15%.

The maximum effect of two of the three optical uncertainties can be estimated. For a manometer tube 2 cm. bore and with a telescope with its objective 62.3 cm. from the axis of the tube and covered to within 1 mm. of the axis we made measurements in which y varied from 0.300 to 0.709 mm. and x from 7.456 to 9.078 mm. The magnification correction, which we applied, varied from -0.0036 to -0.0105 mm. The maximum value of the correction caused by the circle of confusion varied from $+0.0121$ to $+0.0148$ mm.; and the correction for the fact that light was reflected into the telescope from a point lower than that which caused a ray from the top of the light box to be reflected horizontally varied from -0.0010 to -0.0005 mm. The setting error could not be determined but the correction was opposite in sign to that for the circle of confusion and probably constant. It will be noted that the method of computing a eliminates any constant error in y.

(c) *X-ray Shadowgraph Method*

The quantities x and y are determined for the profile curve of a mercury meniscus from an X-ray photograph, and h_0 computed from h and r. These quantities are used to compute a from Tables II and III in which the values of the function $X\ (= x/a)$ (Table II) or $Y\ (= y/a)$ (Table III) are tabulated, the rows being for constant values of the argument $H_0\ (= h_0/a)$ and the columns for constant Y (Table II) or X (Table III). Since H_0 cannot be measured a provisional value is obtained from Table IV by interpolation; this being the value of H_0 for the arguments $X\ (= r/a)$ and $Y\ (= h/a)$ where r and h are measured and the value of a assumed.

Experimental. A photograph of the profile of the meniscus was taken on a plate placed 1.5 cm. in front of the axis of the manometer tube and perpendicular to a beam of X-rays from an aperture 1 mm. in diameter, 1.5 meters behind the manometer tube. The resulting photograph was a shadowgraph of the meniscus and the mercury column without noticeable penumbra. The edge of the dark field surrounding the light image of the meniscus was sharply defined except for a distance of about 0.3 mm. from the right and left ends where the mercury layer presented to the beam of X-rays was thin and the glass layer thick. The profile of the glass tube was also

plainly visible but the contrast was not so sharp as for the mercury.

The plate was aligned on an astronomical plate comparator and the x, y coordinates of the profile curve measured to 0.0001 cm. from the bottom of the meniscus on one side to the bottom of the other, the readings being spaced so that $\Delta x = 1$, 0.5, 0.3, or 0.2 mm. whichever made $\Delta y \lessapprox 0.2$ mm. At the same time the bore and outside diameter of the manometer tube were measured. The outside diameter of the tube was also measured by a micrometer.

The measured quantities are thus: r, h, x_i, y_i $(i = 1, 2, \ldots n)$; all of which are subject to correction for lack of alignment of the plate on the comparator.

Calculations. Plot the measured coördinates of the profile curve on translucent paper to a scale 100 times natural size in the y direction and 25 times in the x direction. Hold the paper to the light and fold so that the two halves of the curve coincide as closely as possible, the two points nearest the bottom of the meniscus on each side being neglected since reproducible settings to 10^{-4} cm. cannot be made in this region. It may happen that there is one more point near the bottom of the meniscus on one side than on the other; if so reject the point nearest the bottom so that there are the same number of points far removed from the axis of the manometer tube on each side. These rejected points are not to be used in any of the following calculations.

The angle θ which the fold makes with the y axis of the cross-section paper is to the first approximation the angle through which the coördinate axes must be rotated and the intersection of the fold with the plot of the profile curve is to the first approximation the proper origin of the coördinate system. The angle θ is positive if the fold slopes upward to the left.

Correct each observed x_i and y_i by the relations:

$$x_i \text{ (corr.)} = [(x_i - x_0) + (y_i - y_0) \tan \theta] \cos \theta, \qquad (i = 1, 2, \ldots n) \quad (6)$$

$$y_i \text{ (corr.)} = [(y_i - y_0) - (x_i - x_0) \tan \theta] \cos \theta,$$

where x_0, y_0 are the coördinates of the proper origin; and multiply each x_i (corr.), y_i (corr.) by the scale factor f which can now be determined as

$$f = \frac{\text{external dia. of tube from micrometer meas.}}{\text{external dia. measured on plate} \times \cos \theta}.$$

The resulting values are: r, h, x_i (from $-r$ to $+r$), y_i (from 0 to h) $(i = 1, 2, \ldots n)$; all of which are corrected to the first approximation for the lack of alignment of the plate on the comparator, the location of the proper origin, and the magnification of the photograph.

Enlarge by interpolation Tables II and III so that there is a row for each increment of 0.0002 in the argument H_0 in the range to be used ($H_0 =$ 0.006 to 0.012 for tubes about 2.0 cm. bore), and a column for each increment of 0.004 in Y (Table II) and 0.025 in X (Table III). The enlarged tables can now be used by linear interpolation.

1. From r, h, and a provisional value of a (say 0.2600 cm.) read from Table IV a provisional value of H_0 corresponding to X $(= r/a)$ and Y $(= h/a)$. Select the row H_0' in Tables II and III having the value of the argument closest to the provisional value just obtained and take $a_1' =$ 0.2600 cm. Compute from the experimental data:

$$X'_{i1} \text{ (obs.)} = x_i/a_1', \qquad (i = 1, 2, \ldots n)$$

$$Y'_{i1} \text{ (obs.)} = y_i/a_1'. \qquad (i = 1, 2, \ldots n)$$

Compute from row H_0' of Tables II and III: Y'_{i1} (calcd.) corresponding to X'_{i1} (obs.) (by direct or inverse interpolation), $(i = 1, 2, \ldots n)$

$$\nu'_{i1} = Y'_{i1} \text{ (obs.)} - Y'_{i1} \text{ (calcd.)} \qquad (i = 1, 2, \ldots n)$$

The final correction for alignment is now to be made. Correct each x_i, y_i by Eq. (6) using

$$\theta = \tan^{-1} \frac{1}{2} \left[\left(\frac{\Sigma_i \nu'_{i1}}{\Sigma_i X'_{i1}} \right)_{x \text{ positive}} + \left(\frac{\Sigma_i \nu'_{i1}}{\Sigma_i X'_{i1}} \right)_{x \text{ negative}} \right], \quad (7)$$

$$x_0 = 0,$$

$$y_0 = \frac{a_1'}{3} \sum_1^3{}_i \nu'_{i1},$$

the last summation being taken for the three points nearest the origin of the coördinate system. In general this final correction will not affect the fourth decimal place in x_i, y_i but serves as a check on the earlier adjustments.

2. Repeat Process (1) if necessary and form:

$\Sigma_i|\nu'_{i1}|$ and $\Sigma_i \nu'_{i1}$ corresponding to H_0' and a_1',

$\Sigma_i|\nu'_{i2}|$ and $\Sigma_i \nu'_{i2}$ corresponding to H_0' and a_2',

etc.;

where all calculations are to be made from the same row H_0' but a is varied in increments of 0.0002 cm. Plot $\Sigma_i|\nu_i'|$ and $\Sigma_i \nu_i'$ each as ordi-

nates against a' as abscissa. The value of a' and $\Sigma_i|\nu_i'|$ for which $\Sigma_i \nu_i' = 0$ are recorded; a' is the capillary constant of the mercury if H_0' happens to be the correct capillary depression of the mercury in the manometer.

3. Repeat Process (2) using the same experimental data—x_i, y_i corrected by Process (1)—but the rows H_0'', H_0''', etc., above and below H_0' in the enlarged table thus obtaining a series of simultaneous value of a and $\Sigma_i|\nu_i|$.

4. Plot $\Sigma_i|\nu_i|$ against a and read the correct value of the capillary constant corresponding to the minimum value of $\Sigma_i|\nu_i|$.

Accuracy. This method gave values of a with a probable error of 0.5% (3 plates). The average difference $n^{-1}\sum_1^n{}_i|Y_i\,(\text{obs.}) - Y_i\,(\text{calcd.})|$ in the fit of the curves was 0.00034 cm. (3 plates).

The last method is by far the most accurate and the most laborious. Much of the work is eliminated if an approximate value of a is known. This may be obtained by either of the first two methods described.

Acknowledgment. We wish to express our thanks to the staff of the Harvard Observatory for making available to us a comparator for measuring the X-ray plates.

5. Summary

The errors introduced into gas thermometric measurements by uncertainties in the capillary depression of mercury and in the volume of the meniscus in the short arm of the manometer are discussed. It is brought out that accurate knowledge of the bore of the manometer tubes, heights of mercury menisci, and the capillary constant of the mercury in the manometer is required to make the necessary corrections.

Methods of determination of the bore of manometer tubes and the elevations of the crown and bottom of a mercury meniscus are discussed.

Three experimental methods for determination of the capillary constant of mercury in manometers which are in use are given.